

D E C L A R A T I O N

I, SHINICHI USUI, a Japanese Patent Attorney registered No. 9694, of Okabe International Patent Office at No. 602, Fuji Bldg., 2-3, Marunouchi 3-chome, Chiyoda-ku, Tokyo, Japan, hereby declare that I have a thorough knowledge of Japanese and English languages, and that the attached pages contain a correct translation into English of the priority documents of Japanese Patent Application No. 2002-310310 filed on October 24, 2002 in the name of CANON KABUSHIKI KAISHA.

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made, are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Signed this 4th day of June, 2008



SHINICHI USUI

PATENT OFFICE
JAPANESE GOVERNMENT

This is to certify that the annexed is a true copy
of the following application as filed with this office.

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Applicant(s): CANON KABUSHIKI KAISHA

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Commissioner,
Patent Office Yasuo IMAI

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Applicant's Information

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[Reference No.] 4771082
[Date] October 24, 2002

[Addressed to] Commissioner of the Patent Office

[International Classification] C12 7/62
G08 5/08

[Title of the Invention] NOVEL POLYHYDROXYALKANOATE CONTAINING UNIT HAVING CARBOXYL GROUP IN SIDE CHAIN WITHIN MOLECULE AND PROCESS FOR PREPARING THE SAME, AND CHARGE CONTROLLING AGENT, TONER BINDER, AND TONER CONTAINING THE NOVEL POLYHYDROXYALKANOATE AND IMAGE FORMING METHOD AND APPARATUS USING THE TONER

[Number of the Claims] 23

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[Prepayment Ledger No.] 089681

[Amount] ¥21,000

[List of Filed Materials]

[Material] Specification 1

[Material] Drawings 1

[Material] Abstract 1

[Proof requirement] necessary

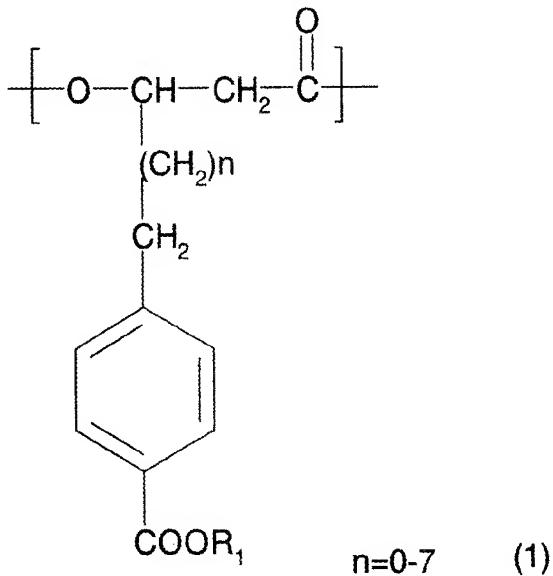
[Name of the Document] Specification

[Title of the Invention] Novel Polyhydroxyalkanoate
Containing Unit Having Carboxyl Group in Side Chain
within Molecule and Process for Preparing the Same, and
5 Charge Controlling Agent, Toner Binder, and Toner
Containing the Novel Polyhydroxyalkanoate and Image
Forming Method and Apparatus Using the Toner

[Claim(s)]

[Claim 1] A polyhydroxyalkanoate containing in a
10 molecule thereof one or more 3-hydroxy- ω -(4-
carboxyphenyl)alkanoic acid units represented by a
chemical formula (1):

[Chemical Formula 1]

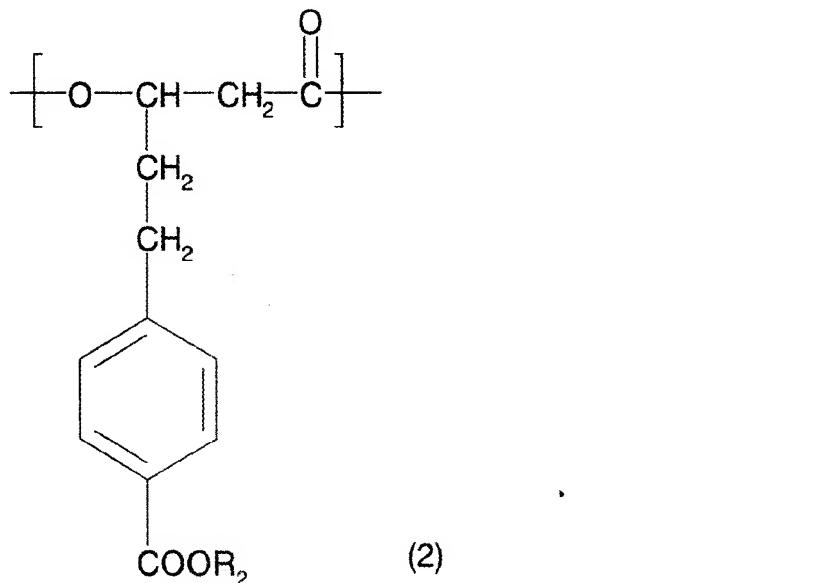


15 wherein n is an integer selected from the range shown
in the chemical formula; R₁ is an H, Na or K atom; and
when more than one unit exists, n and R₁ may differ

from unit to unit, respectively.

[Claim 2] The polyhydroxyalkanoate according to claim 1, wherein the 3-hydroxy- ω -(4-carboxyphenyl)alkanoic acid unit represented by the 5 chemical formula (1) is a 3-hydroxy- ω -(4-carboxyphenyl)valeric acid unit represented by a chemical formula (2):

[Chemical Formula 2]

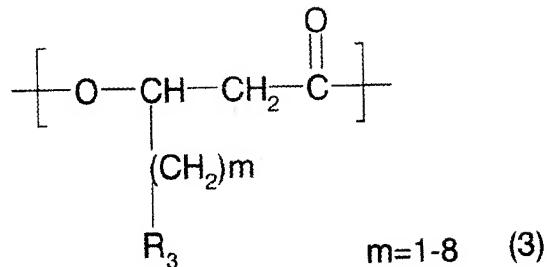


10 wherein R₂ is an H, Na or K atom and, when more than one unit exists, it may differ from unit to unit.

[Claim 3] The polyhydroxyalkanoate according to claim 1 or 2, wherein the polyhydroxyalkanoate contains, besides the 3-hydroxy- ω -(4-carboxyphenyl)alkanoic acid unit represented by the 15 chemical formula (1), at least either a 3-hydroxy- ω -substituted alkanoic acid unit represented by a

chemical formula (3):

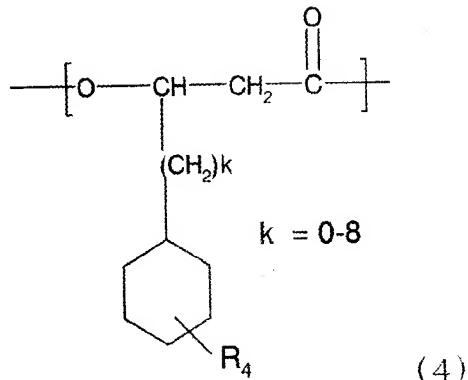
[Chemical Formula 3]



wherein m is an integer selected from the range shown

5 in the chemical formula; R₃ comprises a residue having
a ring structure of either a phenyl or a thiienyl
structure; and when more than one unit exists, m and R₃
may differ from unit to unit, respectively; or

[Chemical Formula 4]



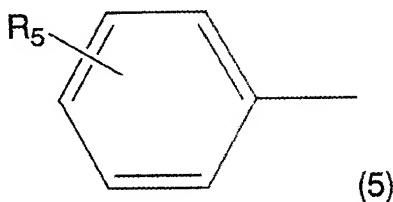
10

wherein R₄ represents a substituent on a cyclohexyl
group and is an H atom, a CN group, an NO₂ group, a
halogen atom, a CH₃ group, a C₂H₅ group, a C₃H₇ group, a
CF₃ group, a C₂F₅ group or a C₃F₇ group; k is an integer
15 selected from 0 to 8; and when more than one unit

exists, k and R₄ may differ from unit to unit.

[Claim 4] The polyhydroxyalkanoate according to any one of claims 1 to 3, wherein R₃ in the chemical formula (3) having a phenyl or thiienyl structure is at least any one selected from the group consisting of residues represented by chemical formula (5), (6), (7), (8), (9), (10), (11), (12), (13), (14) and (15), wherein the chemical formula (5) represents a group consisting of unsubstituted and substituted phenyl groups:

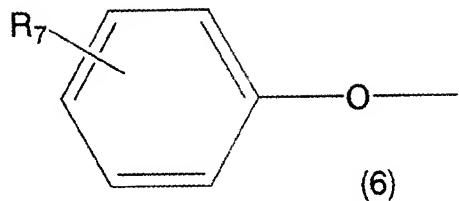
[Chemical Formula 5]



wherein R₅ represents a substituent on the aromatic ring and is an H atom, a halogen atom, a CN group, an NO₂ group, a CH₃ group, a C₂H₅ group, a C₃H₇ group, a CH=CH₂ group, COOR₆ (R₆ represents any one of H, Na and K atoms), a CF₃ group, a C₂F₅ group or a C₃F₇ group; and when more than one unit exists, R₅ may differ from unit to unit;

the chemical formula (6) represents a group consisting of unsubstituted and substituted phenoxy groups:

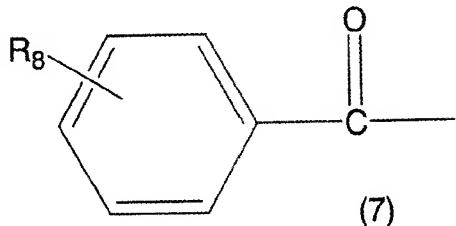
[Chemical Formula 6]



wherein R_7 represents a substituent on the aromatic ring and is an H atom, a halogen atom, a CN group, an NO₂ group, a CH₃ group, a C₂H₅ group, a C₃H₇ group, an 5 SCH₃ group, a CF₃ group, a C₂F₅ group or a C₃F₇ group; and when more than one unit exists, R_7 may differ from unit to unit;

the chemical formula (7) represents a group consisting of unsubstituted and substituted benzoyl groups:

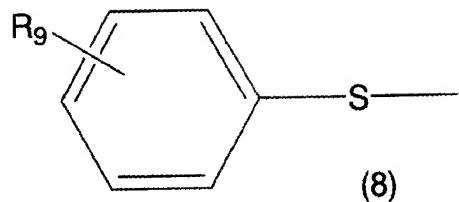
10 [Chemical Formula 7]



wherein R_8 represents a substituent on the aromatic ring and is an H atom, a halogen atom, a CN group, an NO₂ group, a CH₃ group, a C₂H₅ group, a C₃H₇ group, a CF₃ 15 group, a C₂F₅ group or a C₃F₇ group; and when more than one unit exists, R_8 may differ from unit to unit;

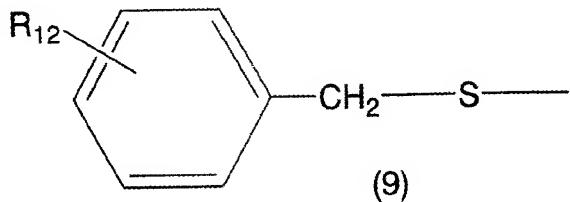
the chemical formula (8) represents a group consisting of unsubstituted and substituted phenylsulfanil groups:

[Chemical Formula 8]



wherein R_9 represents a substituent on the aromatic ring and is an H atom, a halogen atom, a CN group, an NO_2 group, a $COOR_{10}$, an SO_2R_{11} (R_{10} represents any one of 5 an H atom, an Na atom, a K atom, a CH_3 group and a C_2H_5 group and R_{11} represents any one of an OH group, an ONa group, an OK group, a halogen atom, an OCH_3 group and OC_2H_5 group), a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $(CH_3)_2-CH$ group or a $(CH_3)_3-C$ group; and when more than 10 one unit exists, R_9 may differ from unit to unit; the chemical formula (9) represents a group consisting of unsubstituted and substituted (phenylmethyl)sulfanil groups:

[Chemical Formula 9]

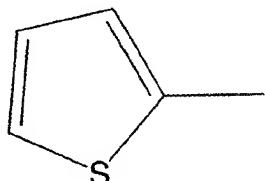


15 wherein R_{12} represents a substituent on the aromatic ring and is an H atom, a halogen atom, a CN group, an NO_2 group, a $COOR_{13}$, an SO_2R_{14} (R_{13} represents any one of an H atom, an Na atom, a K atom, a CH_3 group and a C_2H_5 group and R_{14} represents any one of an OH group, an ONa

group, an OK group, a halogen atom, an OCH_3 group and OC_2H_5 group), a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $(\text{CH}_3)_2\text{-CH}$ group or a $(\text{CH}_3)_3\text{-C}$ group; and when more than one unit exists, R_{12} may differ from unit to unit;

5 the chemical formula (10) represents 2-thienyl group:

[Chemical Formula 10]

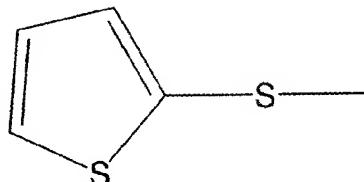


(10)

;

the chemical formula (11) represents a 2-thienylsulfanil group:

10 [Chemical Formula 11]

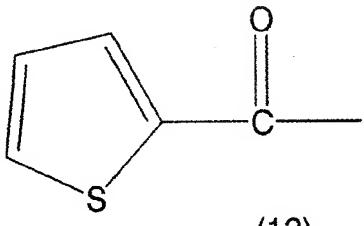


(11)

;

the chemical formula (12) represents a 2-thienylcarbonyl group:

[Chemical Formula 12]

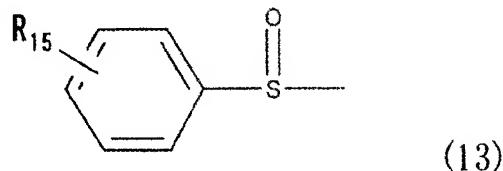


(12)

;

the chemical formula (13) represents a group consisting of unsubstituted and substituted phenylsulfenyl groups:

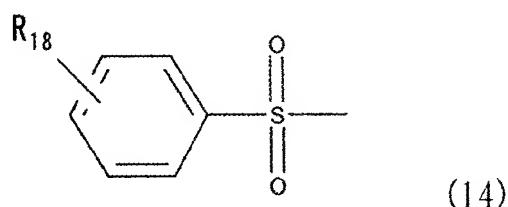
[Chemical Formula 13]



5 wherein R_{15} represents a substituent on the aromatic ring and is an H atom, a halogen atom, a CN group, an NO_2 group, a $COOR_{16}$, an SO_2R_{17} (R_{16} represents any one of an H atom, an Na atom, a K atom, a CH_3 group and a C_2H_5 group and R_{17} represents any one of an OH group, an ONa group, an OK group, a halogen atom, an OCH_3 group and OC_2H_5 group), a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $(CH_3)_2-CH$ group or a $(CH_3)_3-C$ group; and when more than one unit exists, R_{15} may differ from unit to unit;

10 the chemical formula (14) represents a group consisting of unsubstituted and substituted phenylsulfonyl groups:

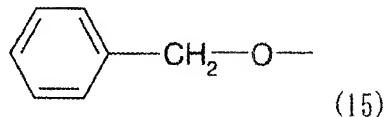
15 [Chemical Formula 14]



wherein R_{18} represents a substituent on the aromatic ring and is an H atom, a halogen atom, a CN group, an NO_2 group, a $COOR_{19}$, an SO_2R_{20} (R_{19} represents any one of

an H atom, an Na atom, a K atom, a CH₃ group and a C₂H₅ group and R₂₀ represents any one of an OH group, an ONa group, an OK group, a halogen atom, an OCH₃ group and OC₂H₅ group), a CH₃ group, a C₂H₅ group, a C₃H₇ group, a (CH₃)₂-CH group or a (CH₃)₃-C group; and when more than one unit exists, R₁₈ may differ from unit to unit; and the chemical formula (15):

[Chemical Formula 15]

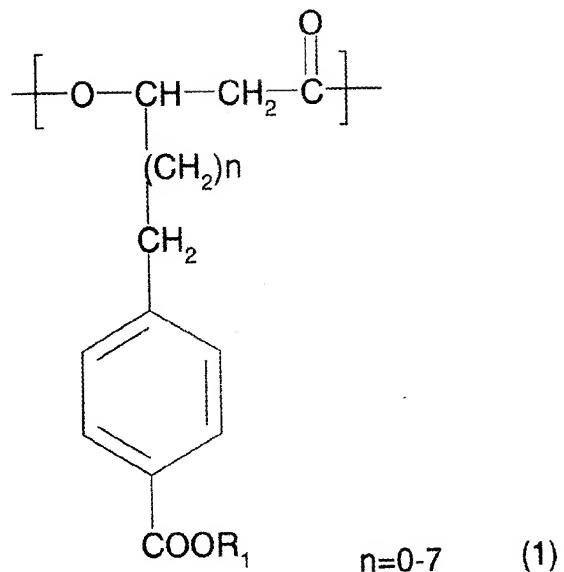


10 represents a group of a (phenylmethyl)oxy group.

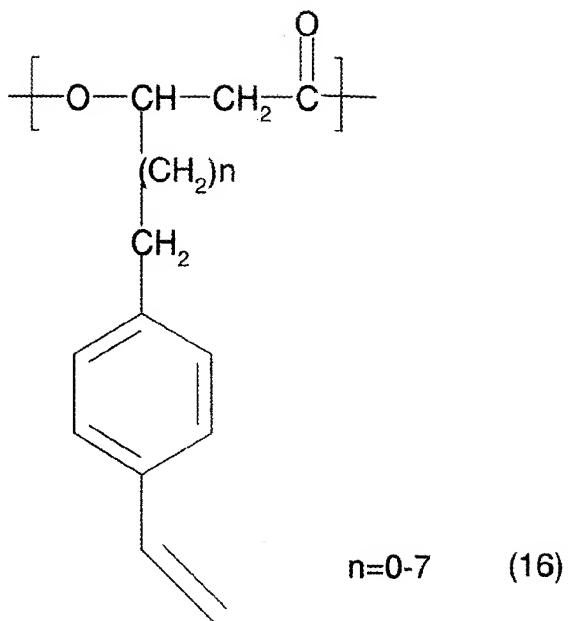
[Claim 5] The polyhydroxyalkanoate according to any one of claims 1 to 4, wherein a number average molecular weight of the polyhydroxyalkanoate is selected to fall in a range of 1000 to 1000000.

15 [Claim 6] A process for preparing a polyhydroxyalkanoate represented by the chemical formula (1):

[Chemical Formula 16]



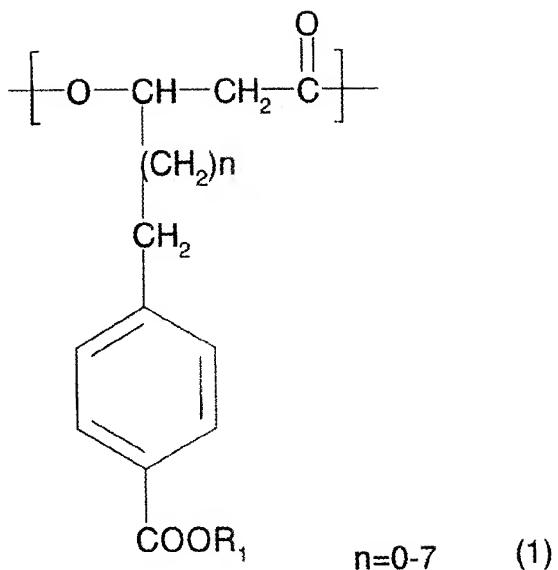
wherein n is an integer selected from the range shown
in the chemical formula; R₁ is an H, Na or K atom; and
when more than one unit exists, n and R₁ may differ
5 from unit to unit,
by oxidizing and cleaving a double bond portion of the
polyhydroxyalkanoate represented by the chemical
formula (16) using a 3-hydroxy-ω-(4-
vinylphenyl)alkanoic acid unit represented by the
10 chemical formula (16) as a raw material
[Chemical Formula 17]



wherein n is an integer selected from 0 to 7; and when more than one unit exists, n may differ from unit to unit.

5 [Claim 7] A process for preparing a polyhydroxyalkanoate comprising at least both 3-hydroxy- ω -(4-carboxyphenyl)alkanoic acid unit represented by the chemical formula (1):

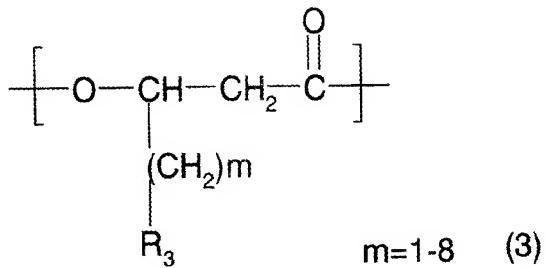
[Chemical Formula 18]



wherein n is an integer selected from the range shown in the formula; R_1 is an H, Na or K atom; and when more than one unit exists, n and R_1 may differ from unit to unit, respectively,

3-hydroxy- ω -substituted alkanoic acid units represented by the chemical formula (3):

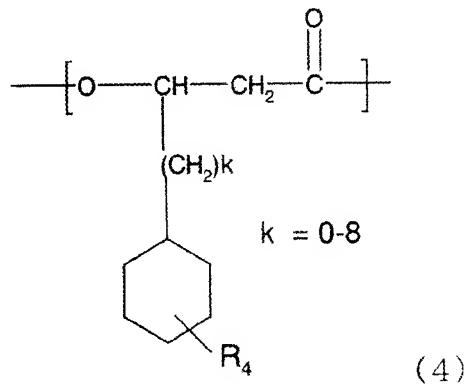
[Chemical Formula 19]



wherein m is an integer selected from the range shown in the chemical formula; R_3 comprises a residue having a ring structure of either a phenyl or a thiienyl

structure; and when more than one unit exists, m and R₃ may differ from unit to unit, respectively, or 3-hydroxy- ω -cyclohexylalkanoic acid units represented by the chemical formula (4):

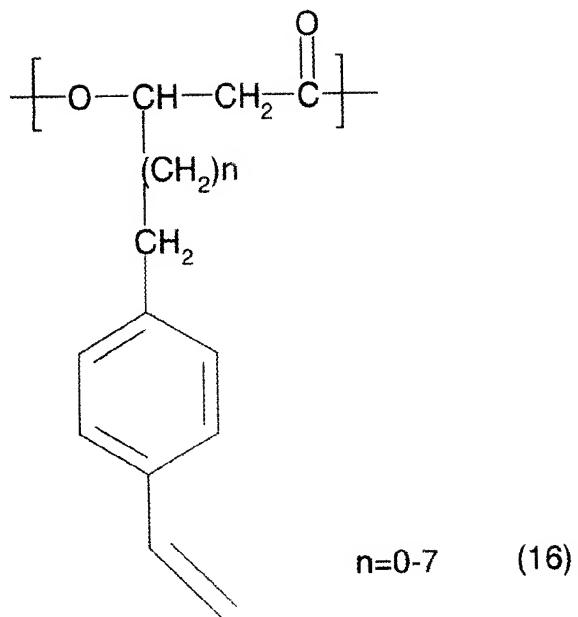
5 [Chemical Formula 20]



wherein R₄ represents a substituent on the cyclohexyl group and is an H atom, a CN group, an NO₂ group, a halogen atom, a CH₃ group, a C₂H₅ group, a C₃H₇ group, a CF₃ group, a C₂F₅ group or C₃F₇ group; k is an integer selected from the range shown in the chemical formula; and when more than one unit exists, R₄ and k may differ from unit to unit, respectively,

10 by oxidizing and cleaving a double bond portion of the
polyhydroxyalkanoate represented by the chemical
15 formula (16) using a 3-hydroxy- ω -(4-vinylphenyl)alkanoic acid unit represented by the
chemical formula (16) as a raw material

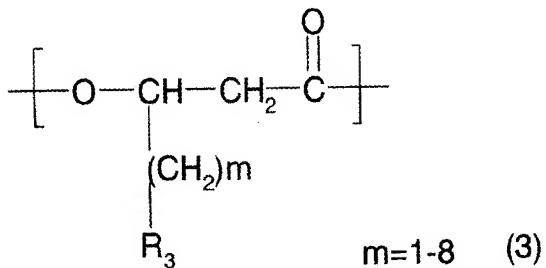
[Chemical Formula 21]



wherein n is an integer selected from 0 to 7, and when more than one unit exists, n may differ from unit to unit,

5 3-hydroxy- ω -substituted alcanoic acid unit represented by the chemical formula (3):

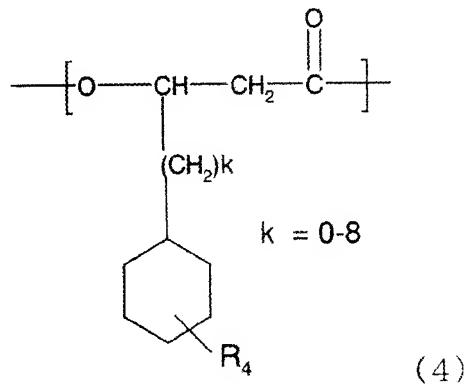
[Chemical Formula 22]



wherein m is an integer selected from the range shown
10 in the chemical formula; R3 comprises a residue having a ring structure of either a phenyl or a thiienyl

structure; and when more than one unit exists, m and R_3 may differ from unit to unit, respectively,
or 3-hydroxy- ω -cyclohexylalkanoic acid units represented by the chemical formula (4):

5 [Chemical Formula 23]

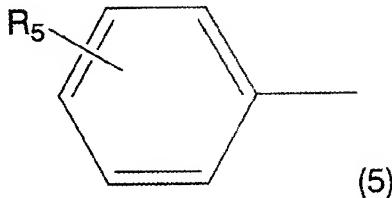


wherein R_4 represents a substituent on the cyclohexyl group and is an H atom, a CN group, an NO_2 group, a halogen atom, a CH_3 group, a C_2H_5 group, a C_3H_7 group, a 10 CF_3 group, a C_2F_5 group or C_3F_7 group; k is an integer selected from the range shown in the formula; and when more than one unit exists, R_4 may differ from unit to unit.

[Claim 8] The process for preparing a
15 polyhydroxyalkanoate according to claim 6 or 7,
characterized in that R_3 in the chemical formula (3),
namely a residue having a phenyl or a thiienyl structure
has at least any one chemical formula selected from the
group consisting of chemical formulae (5), (6), (7),
20 (8), (9), (10), (11), (12), (13), (14) and (15),

wherein the chemical formula (5) is a group consisting of unsubstituted and substituted phenyl groups represented by

[Chemical Formula 24]



(5)

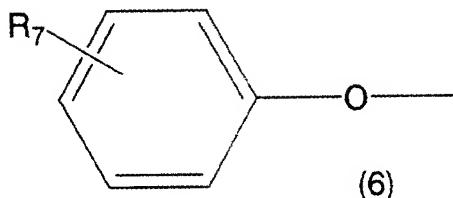
5

wherein R_5 represents a substituent on the aromatic ring and is an H atom, a halogen atom, a CN group, an NO₂ group, a CH₃ group, a C₂H₅ group, a C₃H₇ group, a CH=CH₂ group, COOR₆ (R₆ represents any one of H, Na and K atoms), a CF₃ group, a C₂F₅ group or a C₃F₇ group; and when more than one unit exists, R_5 may differ from unit to unit,

the chemical formula (6) is a group consisting of unsubstituted and substituted phenoxy groups

15 represented by

[Chemical Formula 25]



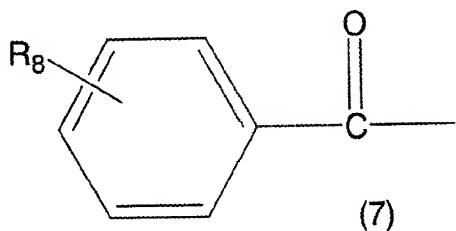
(6)

wherein R_7 represents a substituent on the aromatic ring and is an H atom, a halogen atom, a CN group, an

NO₂ group, a CH₃ group, a C₂H₅ group, a C₃H₇ group, an SCH₃ group, a CF₃ group, a C₂F₅ group or a C₃F₇ group; and when more than one unit exists, R₇ may differ from unit to unit,

5 the chemical formula (7) is a group consisting of unsubstituted and substituted benzoyl groups represented by

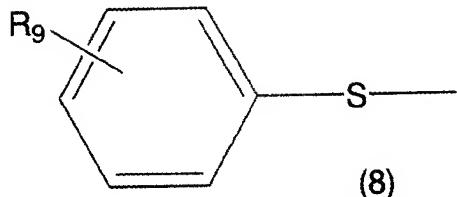
[Chemical Formula 26]



10 wherein R₈ represents a substituent on the aromatic ring and is an H atom, a halogen atom, a CN group, an NO₂ group, a CH₃ group, a C₂H₅ group, a C₃H₇ group, a CF₃ group, a C₂F₅ group or a C₃F₇ group; and when more than one unit exists, R₈ may differ from unit to unit,

15 the chemical formula (8) is a group consisting of unsubstituted and substituted phenylsulfanil groups represented by

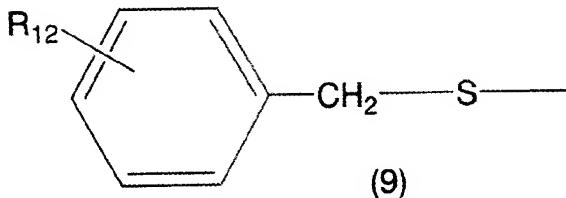
[Chemical Formula 27]



20 wherein R₉ represents a substituent on the aromatic

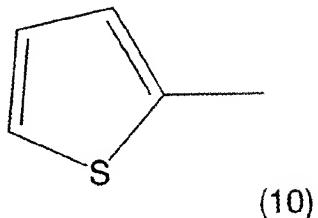
ring and is an H atom, a halogen atom, a CN group, an NO₂ group, a COOR₁₀, an SO₂R₁₁ (R₁₀ represents any one of an H atom, an Na atom, a K atom, a CH₃ group and a C₂H₅ group and R₁₁ represents any one of an OH group, an ONa group, an OK group, a halogen atom, an OCH₃ group and OC₂H₅ group), a CH₃ group, a C₂H₅ group, a C₃H₇ group, a (CH₃)₂-CH group or a (CH₃)₃-C group; and when more than one unit exists, R₉ may differ from unit to unit,
5 the chemical formula (9) is a group consisting of
10 unsubstituted and substituted (phenylmethyl)sulfanil groups represented by

[Chemical Formula 28]



wherein R₁₂ represents a substituent on the aromatic
15 ring and is an H atom, a halogen atom, a CN group, an NO₂ group, a COOR₁₃, an SO₂R₁₄ (R₁₃ represents any one of an H atom, an Na atom, a K atom, a CH₃ group and a C₂H₅ group and R₁₄ represents any one of an OH group, an ONa group, an OK group, a halogen atom, an OCH₃ group and OC₂H₅ group), a CH₃ group, a C₂H₅ group, a C₃H₇ group, a
20 (CH₃)₂-CH group or a (CH₃)₃-C group; and when more than one unit exists, R₁₂ may differ from unit to unit,
the chemical formula (10) is 2-thienyl group
represented by

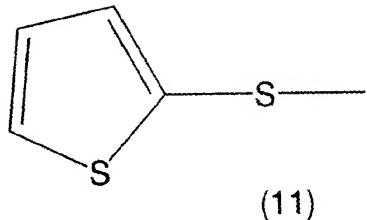
[Chemical Formula 29]



(10)

the chemical formula (11) is 2-thienylsulfanyl group
represented by

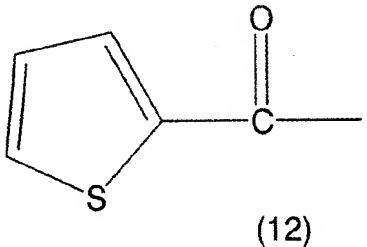
5 [Chemical Formula 30]



(11)

the chemical formula (12) is a 2-thienylcarbonyl group
represented by

[Chemical Formula 31]

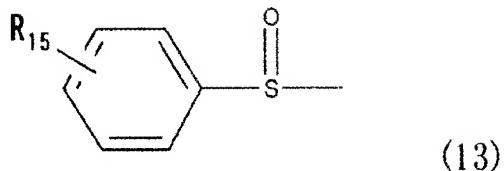


(12)

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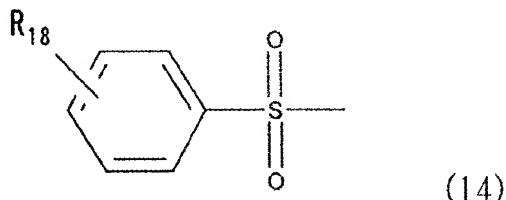
the chemical formula (13) is a group consisting of
unsubstituted and substituted phenylsulfynyl groups
represented by

[Chemical Formula 32]



wherein R_{15} represents a substituent on the aromatic ring and is an H atom, a halogen atom, a CN group, an NO_2 group, a $COOR_{16}$, an SO_2R_{17} (R_{16} represents any one of 5 an H atom, an Na atom, a K atom, a CH_3 group and a C_2H_5 group and R_{17} represents any one of an OH group, an ONa group, an OK group, a halogen atom, an OCH_3 group and OC_2H_5 group), a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $(CH_3)_2-CH$ group or a $(CH_3)_3-C$ group; and when more than 10 one unit exists, R_{15} may differ from unit to unit, the chemical formula (14) is a group consisting of unsubstituted and substituted phenylsulfonyl groups represented by

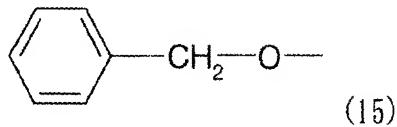
[Chemical Formula 33]



15 wherein R_{18} represents a substituent on the aromatic ring and is an H atom, a halogen atom, a CN group, an NO_2 group, a $COOR_{19}$, an SO_2R_{20} (R_{19} represents any one of 20 an H atom, an Na atom, a K atom, a CH_3 group and a C_2H_5 group and R_{20} represents any one of an OH group, an ONa

group, an OK group, a halogen atom, an OCH_3 group and OC_2H_5 group), a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $(\text{CH}_3)_2\text{-CH}$ group or a $(\text{CH}_3)_3\text{-C}$ group; and when more than one unit exists, R_{18} may differ from unit to unit, and
5 the chemical formula (15) represented by:

[Chemical Formula 34]



is a group of a (phenylmethyl)oxy group.

[Claim 9] The process for preparing a
10 polyhydroxyalkanoate according to any one of claims 6
to 8, wherein the oxidizing and cleaving step is
carried out by using one or more oxidizing agents
selected from the group consisting of permanganate,
bichromate and periodate.

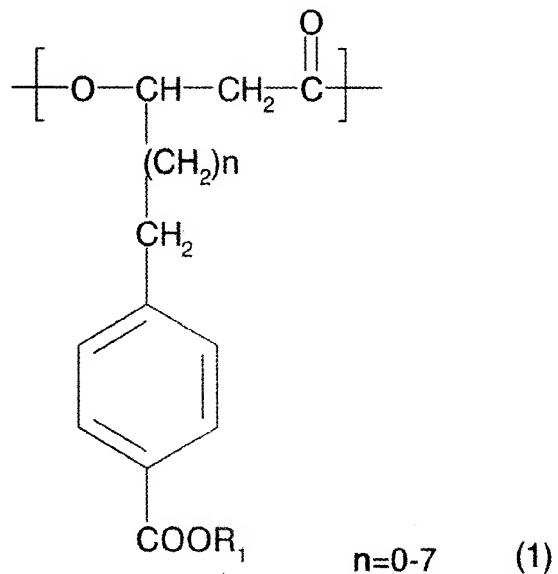
15 [Claim 10] The process for preparing a
polyhydroxyalkanoate according to claim 9, wherein the
oxidizing and cleaving step is carried out by using a
permanganate, as an oxidizing agent, under acid
conditions.

20 [Claim 11] The process for preparing a
polyhydroxyalkanoate according to any one of claims 6
to 8, wherein the oxidizing and cleaving step is
carried out by using ozone.

[Claim 12] A charge controlling agent for
25 controlling a charged state of powder and granular

materials, the agent comprising a polyhydroxyalkanoate that has at least one kind of unit selected from the group consisting of the 3-hydroxy- ω -(4-carboxyphenyl)alkanoic acid units represented by the
5 chemical formula (1):

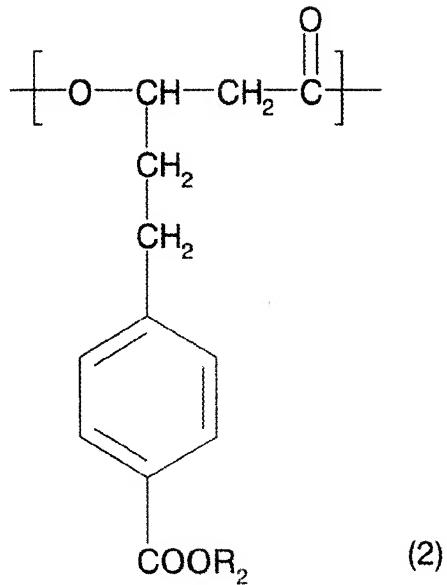
[Chemical Formula 35]



wherein n is an integer selected from the range shown in the chemical formula; R₁ is an H, Na or K atom; and
10 when more than one unit exists, n and R₁ may differ from unit to unit, respectively.

[Claim 13] The charge controlling agent according to claim 12, wherein the 3-hydroxy- ω -(4-carboxyphenyl)alkanoic acid unit represented by the
15 chemical formula (1) is a 3-hydroxy- ω -(4-carboxyphenyl)valeric acid unit represented by a chemical formula (2):

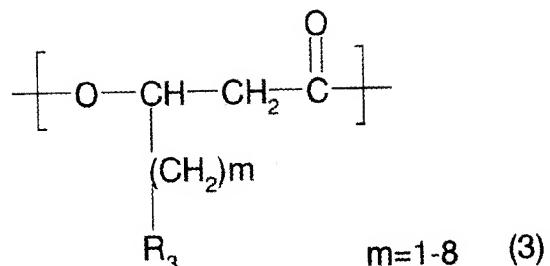
[Chemical Formula 36]



wherein R₂ is an H, Na or K atom and, when more than one unit exists, it may differ from unit to unit.

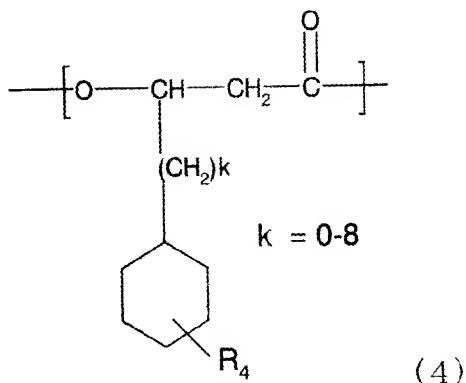
5 [Claim 14] The charge controlling agent according to claim 12 or 13, comprising the polyhydroxyalkanoate which contains, in addition to the 3-hydroxy- ω -(4-carboxyphenyl)alkanoic acid unit represented by the chemical formula (1), either a 3-hydroxy- ω -substituted
10 alkanoic acid unit represented by a chemical formula (3):

[Chemical Formula 37]



wherein m is an integer selected from the range shown in the chemical formula; R_3 comprises a residue having a ring structure of either a phenyl or a thiienyl structure; and when more than one unit exists, m and R_3 may differ from unit to unit, respectively; or

[Chemical Formula 38]

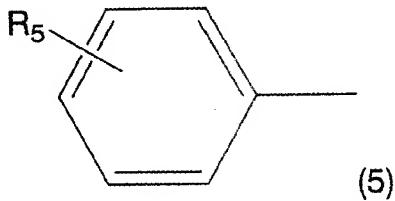


wherein R_4 represents a substituent on a cyclohexyl group and is an H atom, a CN group, an NO_2 group, a halogen atom, a CH_3 group, a C_2H_5 group, a C_3H_7 group, a CF_3 group, a C_2F_5 group or a C_3F_7 group; k is an integer selected from 0 to 8; and when more than one unit exists, k and R_4 may differ from unit to unit.

15 [Claim 15] The charge controlling agent according

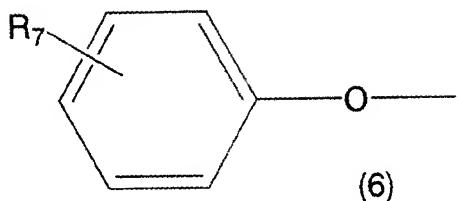
to any one of claims 12 to 14, comprising the polyhydroxyalkanoate wherein R₃ in the chemical formula (3) having a phenyl or thienyl structure is at least any one selected from the group consisting of residues 5 represented by chemical formula (5), (6), (7), (8), (9), (10), (11), (12), (13), (14) and (15), wherein the chemical formula (5) represents a group consisting of unsubstituted and substituted phenyl groups:

10 [Chemical Formula 39]



wherein R₅ represents a substituent on the aromatic ring and is an H atom, a halogen atom, a CN group, an NO₂ group, a CH₃ group, a C₂H₅ group, a C₃H₇ group, a 15 CH=CH₂ group, COOR₆ (R₆ represents any one of H, Na and K atoms), a CF₃ group, a C₂F₅ group or a C₃F₇ group; and when more than one unit exists, R₅ may differ from unit to unit; the chemical formula (6) represents a group consisting 20 of unsubstituted and substituted phenoxy groups:

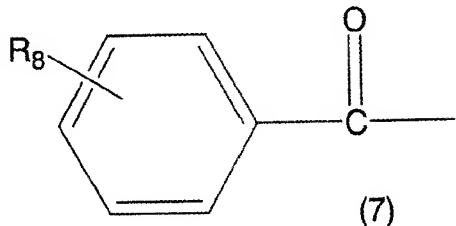
[Chemical Formula 40]



wherein R_7 represents a substituent on the aromatic ring and is an H atom, a halogen atom, a CN group, an NO₂ group, a CH₃ group, a C₂H₅ group, a C₃H₇ group, an 5 SCH₃ group, a CF₃ group, a C₂F₅ group or a C₃F₇ group; and when more than one unit exists, R_7 may differ from unit to unit;

the chemical formula (7) represents a group consisting of unsubstituted and substituted benzoyl groups:

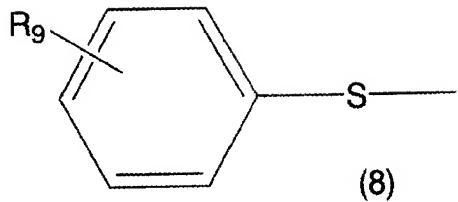
10 [Chemical Formula 41]



wherein R_8 represents a substituent on the aromatic ring and is an H atom, a halogen atom, a CN group, an NO₂ group, a CH₃ group, a C₂H₅ group, a C₃H₇ group, a CF₃ group, a C₂F₅ group or a C₃F₇ group; and when more than 15 one unit exists, R_8 may differ from unit to unit;

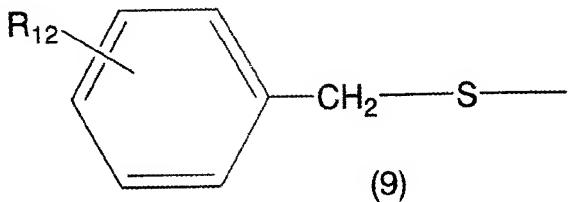
the chemical formula (8) represents a group consisting of unsubstituted and substituted phenylsulfanil groups:

[Chemical Formula 42]



wherein R_9 represents a substituent on the aromatic ring and is an H atom, a halogen atom, a CN group, an NO_2 group, a COOR_{10} , an SO_2R_{11} (R_{10} represents any one of 5 an H atom, an Na atom, a K atom, a CH_3 group and a C_2H_5 group and R_{11} represents any one of an OH group, an ONa group, an OK group, a halogen atom, an OCH_3 group and OC_2H_5 group), a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $(\text{CH}_3)_2\text{-CH}$ group or a $(\text{CH}_3)_3\text{-C}$ group; and when more than 10 one unit exists, R_9 may differ from unit to unit; the chemical formula (9) represents a group consisting of unsubstituted and substituted (phenylmethyl)sulfanil groups:

[Chemical Formula 43]

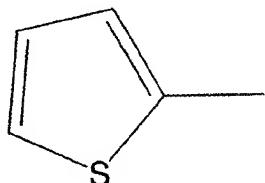


15 wherein R_{12} represents a substituent on the aromatic ring and is an H atom, a halogen atom, a CN group, an NO_2 group, a COOR_{13} , an SO_2R_{14} (R_{13} represents any one of an H atom, an Na atom, a K atom, a CH_3 group and a C_2H_5 group and R_{14} represents any one of an OH group, an ONa

group, an OK group, a halogen atom, an OCH_3 group and OC_2H_5 group), a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $(\text{CH}_3)_2\text{-CH}$ group or a $(\text{CH}_3)_3\text{-C}$ group; and when more than one unit exists, R_{12} may differ from unit to unit;

5 the chemical formula (10) represents 2-thienyl group:

[Chemical Formula 44]

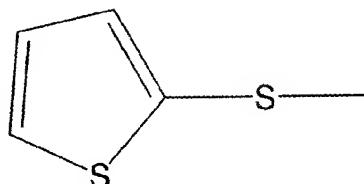


(10)

;

the chemical formula (11) represents a 2-thienylsulfanil group:

10 [Chemical Formula 45]

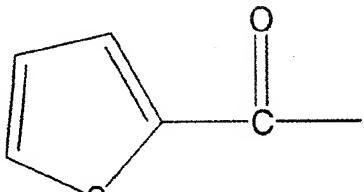


(11)

;

the chemical formula (12) represents a 2-thienylcarbonyl group:

[Chemical Formula 46]

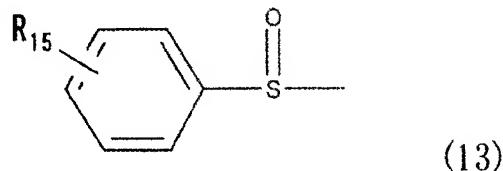


(12)

;

the chemical formula (13) represents a group consisting of unsubstituted and substituted phenylsulfenyl groups:

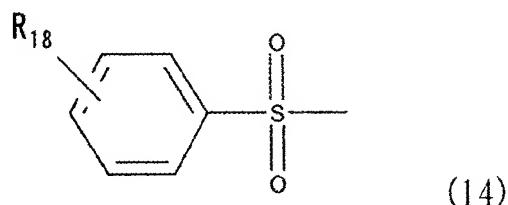
[Chemical Formula 47]



5 wherein R_{15} represents a substituent on the aromatic ring and is an H atom, a halogen atom, a CN group, an NO_2 group, a COOR_{16} , an SO_2R_{17} (R_{16} represents any one of an H atom, an Na atom, a K atom, a CH_3 group and a C_2H_5 group and R_{17} represents any one of an OH group, an ONa group, an OK group, a halogen atom, an OCH_3 group and OC_2H_5 group), a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $(\text{CH}_3)_2\text{-CH}$ group or a $(\text{CH}_3)_3\text{-C}$ group; and when more than one unit exists, R_{15} may differ from unit to unit;

10 the chemical formula (14) represents a group consisting of unsubstituted and substituted phenylsulfonyl groups;

15 [Chemical Formula 48]

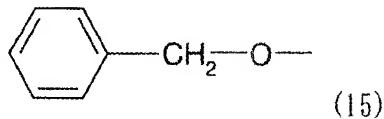


wherein R_{18} represents a substituent on the aromatic ring and is an H atom, a halogen atom, a CN group, an NO_2 group, a COOR_{19} , an SO_2R_{20} (R_{19} represents any one of

20

an H atom, an Na atom, a K atom, a CH₃ group and a C₂H₅ group and R₂₀ represents any one of an OH group, an ONa group, an OK group, a halogen atom, an OCH₃ group and OC₂H₅ group), a CH₃ group, a C₂H₅ group, a C₃H₇ group, a (CH₃)₂-CH group or a (CH₃)₃-C group; and when more than one unit exists, R₁₈ may differ from unit to unit; and the chemical formula (15):

[Chemical Formula 49]



10 represents a group of a (phenylmethyl)oxy group.

[Claim 16] The charge controlling agent according to any one of claims 12 to 15, wherein the powder and granular material is a toner for developing electrostatic latent images.

15 [Claim 17] The charge controlling agent according to any one of claims 12 to 16, wherein a number average molecular weight of the polyhydroxyalkanoate is selected to fall in a range of 1000 to 1000000.

[Claim 18] A toner binder to be used in a toner 20 for developing an electrostatic latent image, containing the charge controlling agent according to any one of claims 12 to 17.

[Claim 19] A toner for developing an electrostatic latent image comprising at least a binder 25 resin, a colorant and a charge controlling agent

according to any one of claims 12 to 17.

[Claim 20] An image forming method comprising at least the steps of:

- charging an electrostatic latent image-holding member by applying voltage to a charging member from outside;
- forming an electrostatic latent image on the charged electrostatic latent image-holding member;
- developing the electrostatic latent image with a toner for developing electrostatic latent images to form a toner image on the electrostatic latent image-holding member;
- transferring the toner image on the electrostatic latent image-holding member to a recording medium; and
- fixing the toner image on the recording medium by heat, wherein the toner for developing an electrostatic latent image comprising at least a binder resin, a colorant and the charge controlling agent according to any one of claims 12 to 17 is used.

20 [Claim 21] The image forming method according to claim 20, comprising at least

the step of charging an electrostatic latent image-holding member by applying voltage to a charging member from outside;

25 the step of forming an electrostatic latent image on the charged electrostatic latent image-holding member;

the step of developing the electrostatic latent image with a toner for developing electrostatic latent images to form a toner image on the electrostatic latent image-holding member;

5 a first transferring step of transferring the toner image on the electrostatic latent image-holding member to an intermediate transfer medium;

10 a second transferring step of transferring the toner image on the intermediate transfer medium to the recording medium; and

fixing the toner image on the recording medium by heat,

wherein the toner for developing an electrostatic latent image comprising at least a binder resin, a
15 colorant and the charge controlling agent according to any one of claims 12 to 17 is used.

[Claim 22] An image forming apparatus comprising at least charging means for charging an electrostatic latent image-holding member by applying voltage to a
20 charging member from outside; electrostatic latent image forming means for forming an electrostatic latent image on the charged electrostatic latent image-holding member; developing means for developing the electrostatic charge image with a toner for developing
25 electrostatic charge images to form a toner image on the electrostatic latent image-holding member; transferring means for transferring the toner image on

the electrostatic latent image-holding member to a recording medium; and fixing means for fixing the toner image on the recording medium by heat, wherein the toner for developing an electrostatic latent image

5 comprising at least a binder resin, a colorant and the charge controlling agent according to any one of claims 12 to 17 is used.

[Claim 23] The image forming apparatus according to claim 22, comprising at least charging means for

10 charging an electrostatic latent image-holding member by applying voltage to a charging member from outside; electrostatic latent image forming means for forming an electrostatic latent image on the charged electrostatic latent image-holding member; developing means for

15 developing the electrostatic charge image with a toner for developing electrostatic charge images to form a toner image on the electrostatic latent image-holding member; a first transferring means for transferring the toner image on the electrostatic latent image-holding

20 member to an intermediate transfer medium; a second transferring means for transferring the toner image on the intermediate transfer medium to the recording medium; and fixing means for fixing the toner image on the recording medium by heat, wherein the toner for

25 developing an electrostatic latent image comprising at least a binder resin, a colorant and the charge controlling agent according to any one of claims 12 to

17 is used.

[Detailed Description of the Invention]

[0001]

[Field of the Invention]

5 The present invention relates to a novel polyhydroxyalkanoate (hereinafter referred to as PHA for short) and a process for preparing the same. More in detail, the present invention relates to a PHA copolymer having a hydrophilic group and a process for
10 preparing the same.

[0002]

Further the present invention relates to a charge controlling agent used in recording methods that utilizes electrophotographic method, electrostatic recording method, magnetic recording method, etc., a toner binder, a toner for developing electrostatic charge images, and image forming method and apparatus that use the toner. Especially, the present invention relates to a charge controlling agent used in an
15 electrophotography, electrostatic recording, and electrostatic printing, such as copiers, printers, and facsimile machines, in which a toner image is formed on an electrostatic latent image bearing member
20 (hereinafter simply referred to as image bearing member) in advance, and then transferred onto a transfer material to form an image, a toner binder, a toner for developing electrostatic charge images, and
25

image forming method and apparatus that use the toner. More in details, the present invention relates to a charge controlling agent having the negative chargeability safer to human bodies and environment, a 5 toner binder which uses it, a toner for developing electrostatic charge images, and image forming method and apparatus that use the toner.

[0003]

[Background Art]

10 (Background Technology in General of Toner)

So far, many methods have been known for electrophotography, and those methods are generally carried out in such a manner that an electric latent image is formed on an image-holding member 15 (photosensitive member) by a variety of means using a photoconductive substance, the latent image is then developed with a toner to form a visible image, and the toner image is transferred onto a transfer material such as a paper as necessary, followed by fixing the 20 toner image on the object transfer material by heat and/or pressure or the like to obtain a copy. For the method for visualizing the electric latent image, a cascade development method, a magnetic brush development method, a pressurizing development method 25 and the like are known. Further, a method using a magnetic toner and a rotary development sleeve with a magnetic pole placed at the center thereof where the

magnetic toner is caused to fly from the development sleeve onto the photoconductor by a magnetic field is also used.

[0004]

5 Development systems for use in development of an electrostatic latent image include a two-component development system using a two-component type developer constituted by a toner and a carrier, and a one-component development system using a one-component type
10 developer constituted only by a toner and using no carrier.

[0005]

Here, the colored fine particle, so-called toner, has a binder resin and a coloring material as essential components, and in addition thereto, magnetic powders and the like as necessary. For the method for imparting an electric charge to the toner, the electrifiability (chargeability) of the binder resin itself may be used without using a charge controlling agent, but in this
15 method, charge stability with time and humidity resistance are compromised, thus making it impossible to obtain high quality images. Therefore, the charge controlling agent is usually added for the purpose of maintaining and controlling the charge of the toner.
20

25 [0006]

Charge controlling agents well known in the art today include, for example, azo dye metal complexes,

aromatic dicarboxylic acid-metal complexes and salicylic acid derivative-metal complexes as negative friction charging agents. In addition, as positive friction charging agents, nigrosine-based dyes,
5 triphenylmethane-based dyes, various types of quaternary ammonium salts and organic tin compounds such as dibutyl tin oxide are known, but toners containing these substances as the charge controlling agent do not necessarily fully satisfy quality
10 characteristics required for the toner such as the electrifiability and stability with time depending on their compositions.

[0007]

For example, a toner containing an azo dye metal complex known as a negative charge controlling agent has an acceptable charge level, but may have reduced dispersibility depending on the type of binder resin to be combined because the azo dye metal complex is a low-molecular crystal. In this case, the negative charge controlling agent is not uniformly distributed in the binder resin, the charge level distribution of the obtained toner is significantly lacking in sharpness, and the obtained image has a low gray-level, resulting in a poor image formation capability. In addition, the azo dye metal complex has a unique color tone, and is thus presently used only for toners having limited colors around black, and if the azo dye metal complex
20
25

is used as a color toner, its lack in clarity as a coloring agent required for obtaining an image having a high level of requirement for the color tone is a serious problem.

5 [0008]

In addition, examples of almost colorless negative charge controlling agents include aromatic dicarboxylic-acid metal complexes, but they may be disadvantageous due to the fact that they are not perfectly colorless, and that they have low dispersibility peculiar to low-molecular-weight crystals.

[0009]

On the other hand, nigrosine based dyes and triphenylmethane based dyes are presently used only for toners having limited colors around black because they are colored themselves, and may be poor in time stability of toners in continuous copying. In addition, conventional quaternary ammonium salts may have insufficient humidity resistance when formed into toners, and in this case, the stability with time may be so poor that high quality images are not provided as they are repeatedly used.

[0010]

25 In addition, in recent years, attention has been given worldwide to reduction of wastes and improvement of safety of wastes in terms of environmental

protection. This problem applies to the field of electrophotography as well. That is, as imaging apparatuses have been widely used, the amounts of wastes of printed papers, discarded toners and copying 5 papers have increased year by year, and the safety of such wastes is important from a viewpoint of protection of global environment.

[0011]

In the light of these problems, polymer charge 10 controlling agents have been studied. Examples are the compounds disclosed in US Patent Nos. 4480021, 4442189, and 4925765 (Patent Documents 1 to 3), Japanese Patent Application Laid-Open Nos. S60-108861, S61-3149, S63-38958, and S63-88564 (Patent Documents 4 to 7).
15 Further, as polymer charge controlling agents that allow toners to exhibit negatively charged characteristics, copolymers of styrene and/or α -methylstyrene with alkyl(meth)acrylate ester or alkyl(meth)acrylate amide having a sulfonic acid group
20 are often used (Japanese Patent Application Laid-Open No. H7-72658, Japanese Patent Application Laid-Open No. H8-179564, Japanese Patent No. 2114410, Japanese Patent No. 2623684, and Japanese Patent No. 2807795; Patent Documents 8 to 12). These materials offer the
25 advantage of being colorless; however, to obtain an intended amount of charge, a large amount of the materials needs to be added.

[0012]

As described above, these compounds do not offer adequate performance as charge controlling agents, and problems of the amount of charge, charge build-up
5 characteristics, stability over time and environment stability arise with them. Further, taking into consideration not only the functions of charge controlling agents, but also their effect on the human body as well as the environment, charge controlling
10 agents are strongly wanted which can be produced using safer compounds by safer and moderate synthesis process and realize the reduction in amount of organic solvent used.

[0013]

15 (Polyhydroxyalkanoate (PHA))

From the aspect of environmental protection, a degradable resin by the action of microorganisms or the like over time, namely a biodegradable resin has been developed. For example, many types of microorganism
20 have been heretofore reported to produce biodegradable resins having a polyester structure (polyhydroxyalkanoate: hereinafter sometimes referred to as PHA) and accumulate in the cell ("Biodegradable Plastic Handbook" edited by Biodegradable Plastics
25 Society, published by N.T.S. Co., Ltd., p. 178-197, 1995). It is known that such PHA may have various compositions and structures depending on the type of

microorganism to be used for the production of the PHA,
the culture medium composition and the culture
conditions, and hitherto studies have been conducted
mainly on control of the composition and structure of
5 PHA to be produced in terms of improvements of physical
properties of PHA.

[0014]

10 [1] First of all, as biosynthesis of PHA obtained
by polymerization of a monomer units with a relatively
simple structure such as 3-hydroxy-n-butyric acid
(hereinafter abbreviated as 3HB), the following can be
pointed out.

[0015]

15 (a) PHA containing 3HB and 3-hydroxy-n-valeric
acid (hereinafter referred to as 3HV)

Japanese Patent Publication Nos. H6-15604, H7-
14352, and H8-19227; and Japanese Patent Application
Laid-Open No. H5-7492 (Patent Documents 13 to 16)

20 (b) PHA containing 3HB and 3-hydroxyhexanoic acid
(hereinafter referred to as 3HHx)

Japanese Patent Application Laid-Open Nos. H5-
93049 and H7-265065 (Patent Documents 17 to 18)

(c) PHA containing 3HB and 4-hyddroxy-n-butyric
acid (hereinafter referred to as 4HB)

25 Japanese Patent Application Laid-Open No. H9-
191893 (Patent Document 19)

(d) PHA containing 3-hydroxyalkanoic acid units of

about 6 to 12 carbon atoms

Japanese Patent No. 2642937 (Patent Document 20)

(e) Biosynthesis using a single aliphatic acid as a carbon source. Products are almost identical to (d).

5 Appl. Environ. Microbiol., 58 (2), 746 (1992) (Non-patent Document 1)

These PHAs are all PHAs that are synthesized via β -oxidation of hydrocarbons or via synthesis of fatty acid from saccharides in microorganisms and consist of 10 monomer units having an alkyl group on their side chains, namely "usual-PHAs."

[0016]

The application of these PHAs has already quite a lot of good records in the field of medical materials.

15 In the agricultural field, biodegradable resins are also used in multi-files, horticulture materials and others, sustained-release agrichemicals, fertilizers, etc. Even in the leisure field, biodegradable resins are used in fishing lines, fishing goods, golf goods 20 and others.

[0017]

However, if considering a wide range of application as a plastic, the above described PHAs are not satisfactory in terms of physical properties, at 25 present. For further expanding the range of, for Example, application of PHA, it is important to conduct a wide range of studies on the improvement of

properties, and for this purpose, development and search of PHA including monomer units of a variety of structures is prerequisite. On the other hand, PHA with a substituent group introduced in the side chain 5 ("unusual PHA") can be expected to be developed as a "functional polymer" with very useful functions and properties originating from the introduced substituent group by selecting the introduced substituent group according to desired characteristics and the like.

10 That is, it is also an important challenge to conduct of development and search of excellent PHA enabling such functionality and biodegradability to be compatible with each other. Examples of substituent groups include groups containing aromatic rings (phenyl 15 group, phenoxy group, etc.), ester groups, unsaturated groups having a double bond on the terminal (alkenyl groups, alkadienyl groups, in particular, allyl groups), cyano groups, halogenated hydrocarbons and epoxide. Among these, especially, the study of PHAs 20 containing aromatic rings has actively been conducted.

[0018]

(a) PHA containing a phenyl group or its partially substituted group

Macromol. Chem. 191, 1957-1965 (1990) and
25 Macromolecules, 24, 5256-5260 (1991) (Non-patent Documents 2 to 3) report that *Pseudomonas oleovorans* produces PHA containing 3-hydroxy-5-phenylvaleric acid

as a unit using 5-phenylvaleric acid as a substrate.

[0019]

Macromolecules, 29, 1762-1766 (1996) (Non-patent Document 4) reports that *Pseudomonas oleovorans* 5 produces PHA containing 3-hydroxy-5-(4'-tolyl) valeric acid as a unit using 5-(4'-tolyl) valeric acid as a substrate.

[0020]

Macromolecules, 32, 2889-2895 (1999) (Non-patent 10 Document 5) reports that *Pseudomonas oleovorans* produces PHA containing 3-hydroxy-5-(2',4'-dinitrophenyl) valeric acid and 3-hydroxy-5-(4'-nitrophenyl) valeric acid as a unit using 5-(2',4'-dinitrophenyl) valeric acid as a substrate.

15 [0021]

(b) PHA containing a phenoxy group or its partially substituted group

Macromol. Chem. Phys., 195, 1665-1672 (1994) (Non-patent Document 6) reports that *Pseudomonas oleovorans* 20 produces PHA copolymer containing 3-hydroxy-5-phenoxyvaleric acid and 3-hydroxy-9-phenoxyundecanoic acid using 11-phenoxyundecanoic acid as a substrate.

[0022]

Japanese Patent No. 2989175 (Patent Document 21) 25 discloses the invention related to a homopolymer consisting of 3-hydroxy-5-(monofluorophenoxy) pentanoate (3H5(MFP)P) units or 3-hydroxy-5-

(difluorophenoxy) pentanoate (3H5(DFP)P) units; a copolymer containing at least (3H5(MFP)P) units or (3H5(DFP)P) units; *Pseudomonas putida* which synthesizes these polymers, and a method of preparing these 5 polymers using the *Pseudomonas* genus. It states that a polymer having a phenoxy group, in which one to two fluorine atoms are substituted on the side chain terminal, can be synthesized by assimilating long chain fatty acid having a substituent group, of which 10 advantage is to provide stereoregularity and water repellency while maintaining a high melting point and good processability.

[0023]

Further, studies are conducted on cyano- 15 substituents and nitro-substituents in addition to the fluorine-substituent described above.

[0024]

Can. J. Microbiol., 41, 32-43 (1995) and Polymer International, 39, 205-213 (1996) (Non-patent Documents 20 7 to 8) report that *Pseudomonas oleovorans* ATCC 29347 and *Pseudomonas putida* KT 2442 produce PHA containing 3-hydroxy-p-cyanophenoxyhexanoic acid or 3-hydroxy-p-nitrophenoxyhexanoic acid as a monomer unit using octanoic acid and p-cyanophenoxyhexanoic acid or p- 25 nitrophenoxyhexanoic acid as substrates.

[0025]

These reports are useful in obtaining polymers

each having an aromatic ring in the side chain of PHA and having properties derived therefrom unlike general PHA whose side chain contains an alkyl group.

[0026]

5 Moreover, as a new category, such studies are conducted that PHA having an appropriate functional group on a side chain is produced to try to produce a new function utilizing the functional group, not only the property change.

10 [0027]

It is reported in Polymer, 41, 1703-1709 (2000) (Non-patent Document 9) that a change of solubility in solvents has been found such that 3-hydroxyalkanoic acid having diol on the side chain terminal, 15 synthesized by an oxidation reaction using potassium permanganate after producing PHA containing as a monomer unit 3-hydroxyalenoic acid having an unsaturated bond in the terminal of the side chain using 10-undecenoic acid as a substrate, is rendered 20 soluble in polar solvents such as methanol, acetone-water mixture (80/20, v/v) and dimethylsulfoxide, and insoluble in nonpolar solvents such as chloroform, tetrahydrofuran and acetone.

[0028]

25 It is reported in Macromolecular chemistry, 4, 289-293 (2001) (Non-patent Document 10) that an improvement in speed of decomposition has been found

for PHA containing 3-hydroxy-9-carboxynonanoic acid as a monomer unit, synthesized by an oxidization and cleavage reaction using potassium permanganate after producing PHA containing as a monomer unit 3-hydroxy-
5 10-undecenoic acid using 10-undecenoic acid as a substrate.

[0029]

However, the PHA in the above report is a copolymer of PHA (usual-PHA) composed of monomer units
10 each having a carboxyl group at the end of its side chain and monomer units each having a straight-chain alkyl group on its side chain (usual PHA). As a result, the problems of low glass transition temperature etc. arise.

15 [0030]

On the other hand, polymers each having an aromatic ring on its side chain are thermally stable and polymers having a carboxylphenyl unit are also expected to have high thermal stability, moreover,
20 their carboxyl group is an active group applicable in various ways; accordingly, these polymers are very useful from the viewpoint of their application as functional materials.

[0031]

25 <Application of Biodegradable Resin to Toner>

Also in the field of electrophotography, the application of a biodegradable resin to a binder resin

has been proposed especially in the toner production. For example, US Patent No. 5004664 (Patent Document 22) discloses a toner that includes, as a constituent, a biodegradable resin, in particular, polyhydroxybutyric acid, polyhydroxyvaleric acid, a copolymer or a blend thereof. In addition, Japanese Patent Application Laid-Open No. H6-289644 (Patent Document 23) discloses an electrophotographic toner particularly for heated roll fixation characterized in that at least the binder resin contains a plant based wax and a biodegradable resin (e.g. polyester produced by microorganism, and natural polymer material of plant or animal origin), and the above described plant based wax is added in the above described binder in an amount of 5 to 50% by weight.

[0032]

Further, Japanese Patent Application Laid-Open No. H7-120975 (Patent Document 24) discloses a toner for electrophotography characterized by containing lactic acid based resin as a binder resin. Furthermore, there is disclosed in Japanese Patent Application Laid-Open No. H9-274335 (Patent Document 25) a toner for developing electrostatic charge images that is characterized by including: a polyester resin, which is obtained by subjecting a composition containing lactic acid and oxycarboxylic acid of three or more functional groups to dehydration polycondensation; and a colorant.

[0033]

In addition, Japanese Patent Application Laid-Open No. H8-262796 (Patent Document 26) discloses an electrophotographic toner containing a binder resin and 5 a coloring agent, characterized in that the binder resin is composed of a biodegradable resin (e.g. aliphatic polyester resin), and the coloring agent is composed of non-water soluble pigments. Further, there is disclosed in Japanese Patent Application Laid-Open 10 No. H9-281746 (Patent Document 27) a toner for developing electrostatic charge images that is characterized by including: a urethane polyester resin, which is obtained by cross-linking polylactic acid with a polyvalent isocyanate of three or more functional 15 groups; and a colorant.

[0034]

All of the toners for electrophotography described above use biodegradable resins as their binder resin and are recognized to produce the effect of 20 contributing to the environmental conservation.

[0035]

However, there has been known no report about the use of a biodegradable resin for a charge controlling agent, and there is still great room for improvement of 25 charge controlling agent in view of the environmental conservation etc.

[0036]

In the invention of this application, the microorganisms described in Japanese Patent Application Laid-Open No. 2001-288256 (Patent Document 28) are used. The other techniques related to the invention of 5 this application include, for example, techniques for obtaining carboxylic acid by cleaving carbon-carbon double bonds with an oxidizing agent (Patent Document 29, Non-patent Documents 11 to 14).

[0037]

10 [Patent Document 1] U.S. Patent No. 4480021
[Patent Document 2] U.S. Patent No. 4442189
[Patent Document 3] U.S. Patent No. 4925765
[Patent Document 4] Japanese Patent Application
Laid-Open No. S60-108861

15 [Patent Document 5] Japanese Patent Application
Laid-Open No. S61-3149
[Patent Document 6] Japanese Patent Application
Laid-Open No. S63-38958
[Patent Document 7] Japanese Patent Application

20 Laid-Open No. S63-88564
[Patent Document 8] Japanese Patent Application
Laid-Open No. H7-72658
[Patent Document 9] Japanese Patent Application
Laid-Open No. H8-179564

25 [Patent Document 10] Japanese Patent No. 2114410
[Patent Document 11] Japanese Patent No. 2623684
[Patent Document 12] Japanese Patent No. 2807795

[Patent Document 13] Japanese Patent Publication
No. H6-15604

[Patent Document 14] Japanese Patent Publication
No. H7-14352

5 [Patent Document 15] Japanese Patent Publication
No. H8-19227

[Patent Document 16] Japanese Patent Application
Laid-Open No. H5-7492

[Patent Document 17] Japanese Patent Application
10 Laid-Open No. H5-93049

[Patent Document 18] Japanese Patent Application
Laid-Open No. H7-265065

[Patent Document 19] Japanese Patent Application
Laid-Open No. H9-191893

15 [Patent Document 20] Japanese Patent No. 2642937

[Patent Document 21] Japanese Patent No. 2989175

[Patent Document 22] U.S. Patent No. 5004664

[Patent Document 23] Japanese Patent Application
Laid-Open No. H6-289644

20 [Patent Document 24] Japanese Patent Application
Laid-Open No. H7-120975

[Patent Document 25] Japanese Patent Application
Laid-Open No. H9-274335

[Patent Document 26] Japanese Patent Application
25 Laid-Open No. H8-262796

[Patent Document 27] Japanese Patent Application
Laid-Open No. H9-281746

[Patent Document 28] Japanese Patent Application
Laid-Open No. 2001-288256

[Patent Document 29] Japanese Patent Application
Laid-Open No. S59-190945

5 [Non-patent Document 1] *Appl. Environ. Microbiol.*,
58 (2), 746 (1992)

[Non-patent Document 2] *Macromol. Chem.* 191, 1957-
1965 (1990)

[Non-patent Document 3] *Macromolecules*, 24, 5256-
10 5260 (1991)

[Non-patent Document 4] *Macromolecules*, 29, 1762-
1766 (1996)

[Non-patent Document 5] *Macromolecules*, 32, 2889-
2895 (1999)

15 [Non-patent Document 6] *Macromol. Chem. Phys.*,
195, 1665-1672 (1994)

[Non-patent Document 7] *Can. J. Microbiol.*, 41,
32-43 (1995)

[Non-patent Document 8] *Polymer International*, 39,
20 205-213 (1996)

[Non-patent Document 9] *Polymer*, 41, 1703-1709
(2000)

[Non-patent Document 10] *Macromolecular chemistry*,
4, 289-293 (2001)

25 [Non-patent Document 11] *J. Chem. Soc., Perkin.
Trans. 1*, 806 (1973)

[Non-patent Document 12] *Org. Synth.*, 4, 698

(1963)

[Non-patent Document 13] J. Org. Chem., 46, 19

(1981)

[Non-patent Document 14] J. Am. Chem. Soc., 81,

5 4273 (1959)

[0038]

[Problem to be Solved by the Invention]

A polyester obtained by subjecting to a chemical reaction/treatment a polyester having the vinyl group reported so far can be given a variety of functions, but does not necessarily have satisfactory thermal characteristics because of the existence of a middle to long alkyl chain in the side chain. That is, the glass transition temperature and melting point of the polyester is low, resulting in significant limitations to the range of applications as moldings and films.

[0039]

On the other hand, a polyester having an aromatic ring on the side chain generally has a high melting point and thus finds a wide range of applications as moldings and films as described previously. However, the polyhydroxyalkanoate type polyester having units each containing an aromatic ring substituted with a functional group capable of enduring a variety of applications includes only examples described above, and further more functional polyhydroxyalkanoate type polyesters have been desired.

[0040]

This invention is made to solve the above described problems; accordingly, the object of this invention is to provide a polyhydroxyalkanoate-type 5 polyester having a unit that includes an aromatic ring whose hydrogen is substituted with a carboxyl group, a functional group used for various applications, and a process for preparing the same.

[0041]

10 In addition, in order to solve the above described problems, the present invention provides a negatively charged charge controlling agent, being more contributable to preservation of environments and the like, and having high performance (high charge level, 15 quick start of charge, excellent stability with time, and high environmental stability) and improved dispersibility in the aspect of functionality, a toner binder containing the charge controlling agent, an electrostatic latent image developing toner containing 20 the charge controlling agent, and an image formation method and an image forming apparatus using the electrostatic latent image developing toner.

[0042]

[Means for Solving the Problem]

25 After intensive research effort for solving the above described problems, the inventors of this invention have found that a polyhydroxyalkanoate type

polyester having a unit that includes an aromatic ring substituted with a carboxyl group, a functional group used for various applications can be produced by reacting a polyhydroxyalkanoate type polyester

5 including a unit that has a vinylphenyl structure with various compounds that serve the objectives.

[0043]

In addition, after intensive research effort for achieving the above described objectives, the inventors
10 have found that the above PHA has excellent characteristics as a charge controlling agent, and has a high level of safety for human bodies and environments, and that a significant effect can be exhibited when an electrostatic latent image developing
15 toner (hereinafter referred to toner) containing the charge controlling agent and the toner are used in an image forming apparatus having a certain development system.

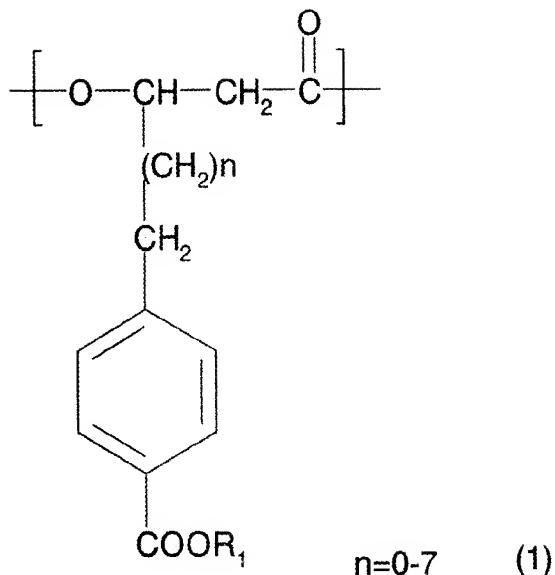
The summary of this invention is as follows.

20 [0044]

[1] A polyhydroxyalkanoate containing in a molecule thereof one or more 3-hydroxy- ω -(4-carboxyphenyl)alkanoic acid units represented by a chemical formula (1):

25 [0045]

[Chemical Formula 50]



[0046]

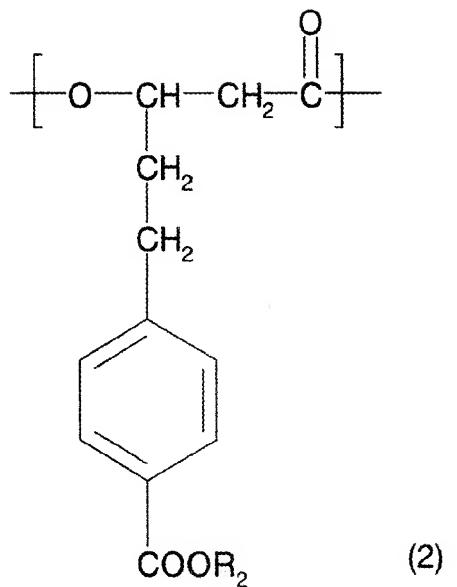
wherein n is an integer selected from the range shown in the chemical formula; R₁ is an H, Na or K atom; and
5 when more than one unit exists, n and R₁ may differ from unit to unit, respectively.

[0047]

[2] The polyhydroxyalkanoate according to [1], wherein the 3-hydroxy-ω-(4-carboxyphenyl)alkanoic acid
10 unit represented by the chemical formula (1) is a 3-hydroxy-ω-(4-carboxyphenyl)valeric acid unit represented by a chemical formula (2):

[0048]

[Chemical Formula 51]



[0049]

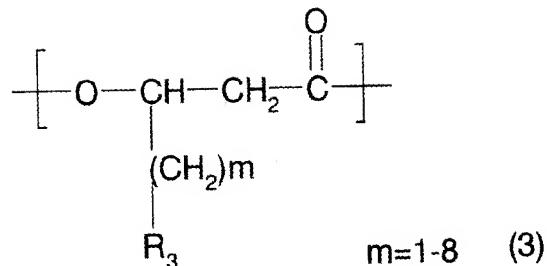
wherein R₂ is an H, Na or K atom and, when more than one unit exists, it may differ from unit to unit.

5 [0050]

[3] The polyhydroxyalkanoate according to [1] or [2], wherein the polyhydroxyalkanoate contains, besides the 3-hydroxy-ω-(4-carboxyphenyl)alkanoic acid unit represented by the chemical formula (1), at least
10 either a 3-hydroxy-ω-substituted alkanoic acid unit represented by a chemical formula (3):

[0051]

[Chemical Formula 52]

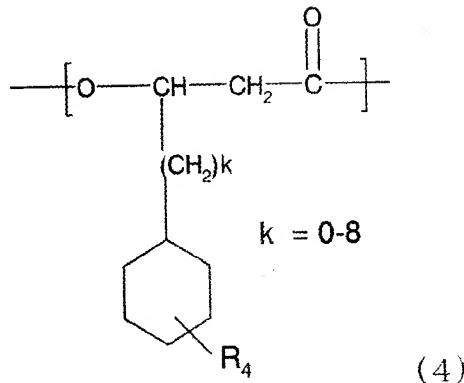


[0052]

wherein m is an integer selected from the range shown in the chemical formula; R_3 comprises a residue having
5 a ring structure of either a phenyl or a thiienyl structure; and when more than one unit exists, m and R_3 may differ from unit to unit, respectively; or

[0053]

[Chemical Formula 53]



10

[0054]

wherein R_4 represents a substituent on a cyclohexyl group and is an H atom, a CN group, an NO_2 group, a halogen atom, a CH_3 group, a C_2H_5 group, a C_3H_7 group, a
15 CF_3 group, a C_2F_5 group or a C_3F_7 group; k is an integer

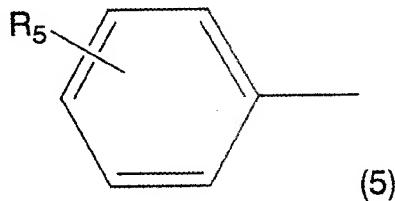
selected from 0 to 8; and when more than one unit exists, k and R₄ may differ from unit to unit.

[0055]

[4] The polyhydroxyalkanoate according to any one
5 of [1] to [3], wherein R₃ in the chemical formula (3)
having a phenyl or thienyl structure is at least any
one selected from the group consisting of residues
represented by chemical formula (5), (6), (7), (8),
(9), (10), (11), (12), (13), (14) and (15),
10 wherein the chemical formula (5) represents a group
consisting of unsubstituted and substituted phenyl
groups:

[0056]

[Chemical Formula 54]



(5)

15

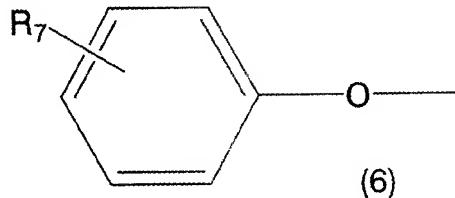
[0057]

wherein R₅ represents a substituent on the aromatic
ring and is an H atom, a halogen atom, a CN group, an
NO₂ group, a CH₃ group, a C₂H₅ group, a C₃H₇ group, a
20 CH=CH₂ group, COOR₆ (R₆ represents any one of H, Na and
K atoms), a CF₃ group, a C₂F₅ group or a C₃F₇ group; and
when more than one unit exists, R₅ may differ from unit
to unit;

the chemical formula (6) represents a group consisting of unsubstituted and substituted phenoxy groups:

[0058]

[Chemical Formula 55]



5

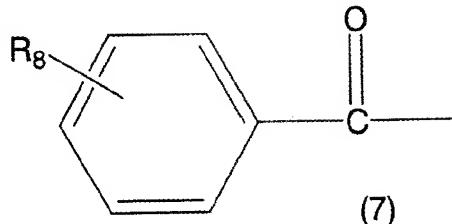
[0059]

wherein R_7 represents a substituent on the aromatic ring and is an H atom, a halogen atom, a CN group, an NO₂ group, a CH₃ group, a C₂H₅ group, a C₃H₇ group, an 10 SCH₃ group, a CF₃ group, a C₂F₅ group or a C₃F₇ group; and when more than one unit exists, R_7 may differ from unit to unit;

the chemical formula (7) represents a group consisting of unsubstituted and substituted benzoyl groups:

15 [0060]

[Chemical Formula 56]



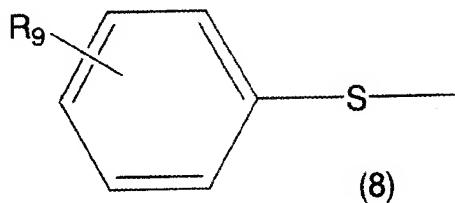
[0061]

wherein R_8 represents a substituent on the aromatic

ring and is an H atom, a halogen atom, a CN group, an NO₂ group, a CH₃ group, a C₂H₅ group, a C₃H₇ group, a CF₃ group, a C₂F₅ group or a C₃F₇ group; and when more than one unit exists, R₉ may differ from unit to unit;

5 the chemical formula (8) represents a group consisting of unsubstituted and substituted phenylsulfanil groups:
[0062]

[Chemical Formula 57]

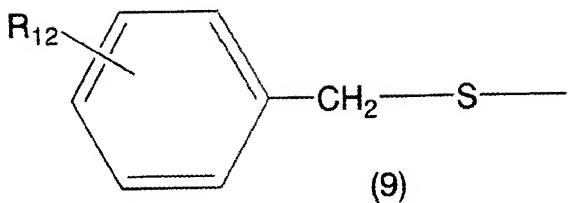


10 [0063]

wherein R₉ represents a substituent on the aromatic ring and is an H atom, a halogen atom, a CN group, an NO₂ group, a COOR₁₀, an SO₂R₁₁ (R₁₀ represents any one of an H atom, an Na atom, a K atom, a CH₃ group and a C₂H₅ group and R₁₁ represents any one of an OH group, an ONa group, an OK group, a halogen atom, an OCH₃ group and OC₂H₅ group), a CH₃ group, a C₂H₅ group, a C₃H₇ group, a (CH₃)₂-CH group or a (CH₃)₃-C group; and when more than one unit exists, R₉ may differ from unit to unit;

15 the chemical formula (9) represents a group consisting of unsubstituted and substituted (phenylmethyl)sulfanil groups:
[0064]

[Chemical Formula 58]

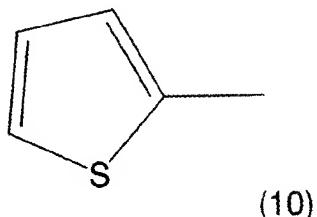


[0065]

wherein R_{12} represents a substituent on the aromatic ring and is an H atom, a halogen atom, a CN group, an NO₂ group, a COOR₁₃, an SO₂R₁₄ (R₁₃ represents any one of an H atom, an Na atom, a K atom, a CH₃ group and a C₂H₅ group and R₁₄ represents any one of an OH group, an ONa group, an OK group, a halogen atom, an OCH₃ group and OC₂H₅ group), a CH₃ group, a C₂H₅ group, a C₃H₇ group, a (CH₃)₂-CH group or a (CH₃)₃-C group; and when more than one unit exists, R₁₂ may differ from unit to unit; the chemical formula (10) represents 2-thienyl group:

[0066]

[Chemical Formula 59]



15

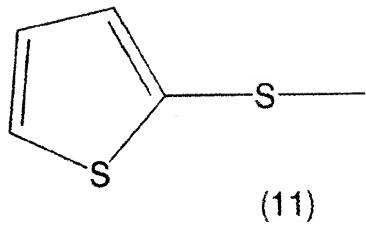
;

[0067]

the chemical formula (11) represents a 2-thienylsulfanil group:

[0068]

20 [Chemical Formula 60]



(11)

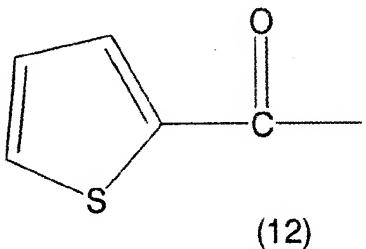
;

[0069]

the chemical formula (12) represents a 2-thienylcarbonyl group:

5 [0070]

[Chemical Formula 61]



(12)

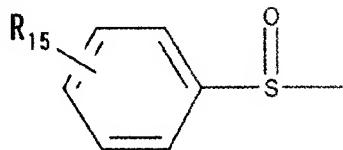
;

[0071]

the chemical formula (13) represents a group consisting
10 of unsubstituted and substituted phenylsulfenyl groups:

[0072]

[Chemical Formula 62]



(13)

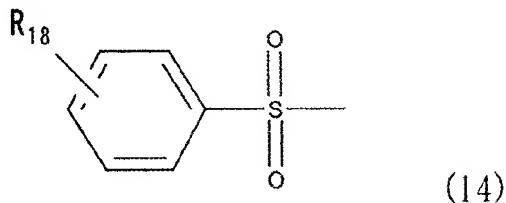
[0073]

15 wherein R₁₅ represents a substituent on the aromatic
ring and is an H atom, a halogen atom, a CN group, an

NO₂ group, a COOR₁₆, an SO₂R₁₇ (R₁₆ represents any one of an H atom, an Na atom, a K atom, a CH₃ group and a C₂H₅ group and R₁₇ represents any one of an OH group, an ONa group, an OK group, a halogen atom, an OCH₃ group and 5 OC₂H₅ group), a CH₃ group, a C₂H₅ group, a C₃H₇ group, a (CH₃)₂-CH group or a (CH₃)₃-C group; and when more than one unit exists, R₁₅ may differ from unit to unit; the chemical formula (14) represents a group consisting of unsubstituted and substituted phenylsulfonyl groups:

10 [0074]

[Chemical Formula 63]

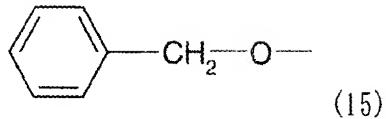


[0075]

wherein R₁₈ represents a substituent on the aromatic 15 ring and is an H atom, a halogen atom, a CN group, an NO₂ group, a COOR₁₉, an SO₂R₂₀ (R₁₉ represents any one of an H atom, an Na atom, a K atom, a CH₃ group and a C₂H₅ group and R₂₀ represents any one of an OH group, an ONa group, an OK group, a halogen atom, an OCH₃ group and 20 OC₂H₅ group), a CH₃ group, a C₂H₅ group, a C₃H₇ group, a (CH₃)₂-CH group or a (CH₃)₃-C group; and when more than one unit exists, R₁₈ may differ from unit to unit; and the chemical formula (15):

[0076]

[Chemical Formula 64]



[0077]

5 represents a group of a (phenylmethyl)oxy group.

[0078]

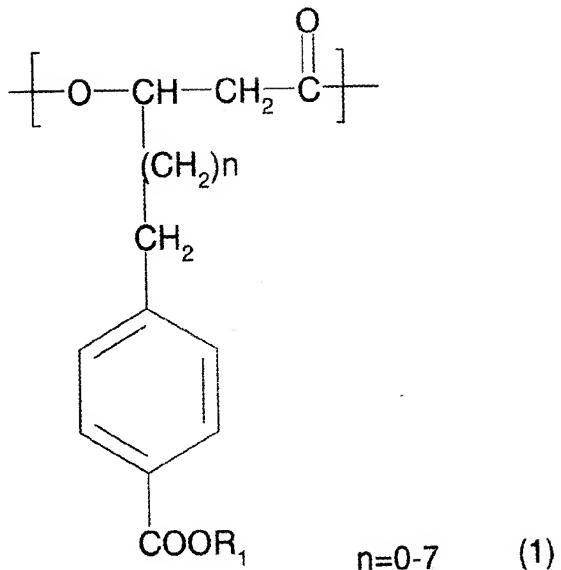
[5] The polyhydroxyalkanoate according to any one
of [1] to [4], wherein a number average molecular
weight of the polyhydroxyalkanoate is selected to fall
10 in a range of 1000 to 1000000.

[0079]

[6] A process for preparing a
polyhydroxyalkanoate represented by the chemical
formula (1):

15 [0080]

[Chemical Formula 65]

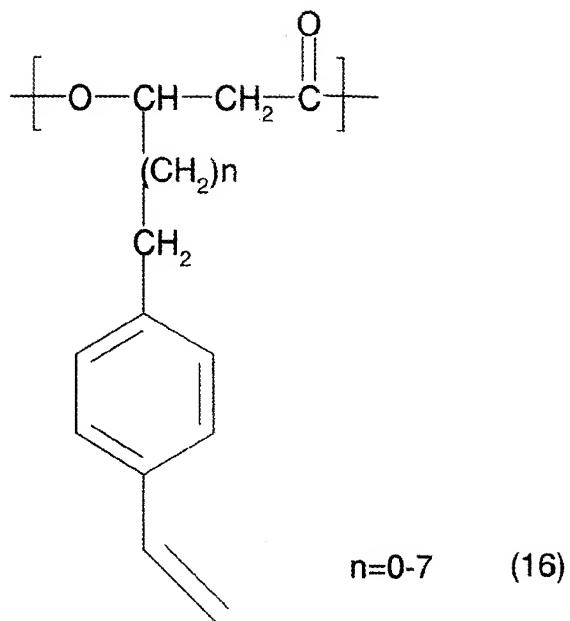


[0081]

wherein n is an integer selected from the range shown
in the chemical formula; R₁ is an H, Na or K atom; and
5 when more than one unit exists, n and R₁ may differ
from unit to unit,
by oxidizing and cleaving a double bond portion of the
polyhydroxyalkanoate represented by the chemical
formula (16) using a 3-hydroxy-ω-(4-
10 vinylphenyl)alkanoic acid unit represented by the
chemical formula (16) as a raw material

[0082]

[Chemical Formula 66]



[0083]

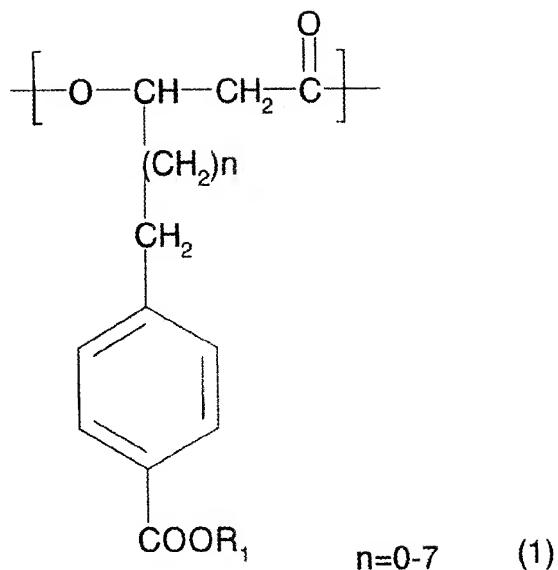
wherein n is an integer selected from 0 to 7; and when
more than one unit exists, n may differ from unit to
5 unit.

[0084]

[7] A process for preparing a
polyhydroxyalkanoate comprising at least both 3-
hydroxy- ω -(4-carboxyphenyl)alkanoic acid unit
10 represented by the chemical formula (1):

[0085]

[Chemical Formula 67]



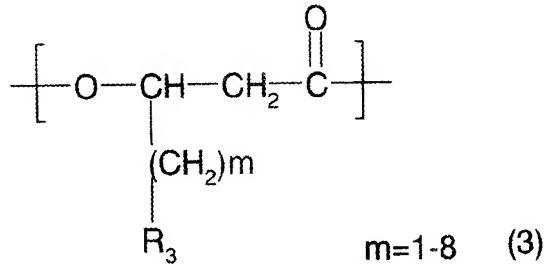
[0086]

wherein n is an integer selected from the range shown in the formula; R₁ is an H, Na or K atom; and when more than one unit exists, n and R₁ may differ from unit to unit, respectively,

3-hydroxy- ω -substituted alkanoic acid units represented by the chemical formula (3):

[0087]

10 [Chemical Formula 68]

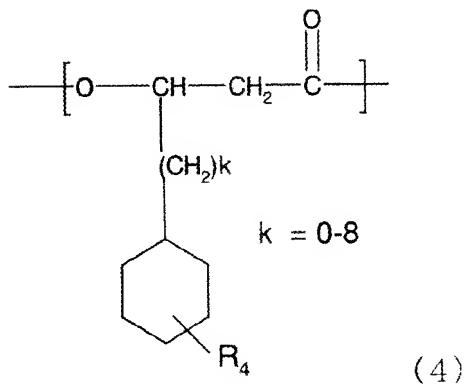


[0088]

wherein m is an integer selected from the range shown in the chemical formula; R₃ comprises a residue having a ring structure of either a phenyl or a thiienyl structure; and when more than one unit exists, m and R₃ 5 may differ from unit to unit, respectively, or 3-hydroxy-ω-cyclohexylalkanoic acid units represented by the chemical formula (4):

[0089]

[Chemical Formula 69]



10

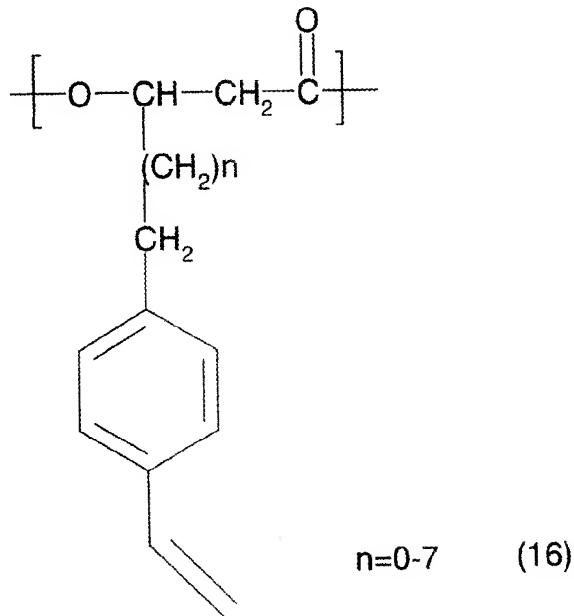
[0090]

wherein R₄ represents a substituent on the cyclohexyl group and is an H atom, a CN group, an NO₂ group, a halogen atom, a CH₃ group, a C₂H₅ group, a C₃H₇ group, a 15 CF₃ group, a C₂F₅ group or C₃F₇ group; k is an integer selected from the range shown in the chemical formula; and when more than one unit exists, R₄ and k may differ from unit to unit, respectively, by oxidizing and cleaving a double bond portion of the 20 polyhydroxyalkanoate represented by the chemical

formula (16) using a 3-hydroxy- ω -(4-vinylphenyl)alkanoic acid unit represented by the chemical formula (16) as a raw material

[0091]

5 [Chemical Formula 70]



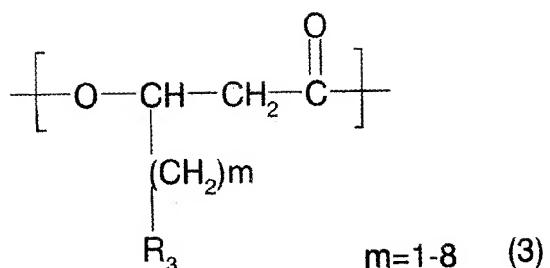
[0092]

wherein n is an integer selected from 0 to 7, and when more than one unit exists, n may differ from unit to
10 unit,

3-hydroxy- ω -substituted alkanoic acid unit represented by the chemical formula (3):

[0093]

[Chemical Formula 71]

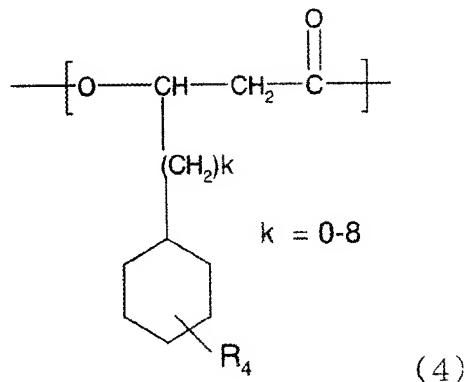


[0094]

wherein m is an integer selected from the range shown in the chemical formula; R_3 comprises a residue having
5 a ring structure of either a phenyl or a thiienyl structure; and when more than one unit exists, m and R_3 may differ from unit to unit, respectively, or 3-hydroxy- ω -cyclohexylalkanoic acid units represented by the chemical formula (4):

10 [0095]

[Chemical Formula 72]



[0096]

wherein R_4 represents a substituent on the cyclohexyl group and is an H atom, a CN group, an NO_2 group, a
15 halogen atom, a CH_3 group, a C_2H_5 group, a C_3H_7 group, a

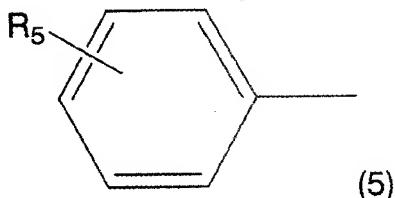
CF₃ group, a C₂F₅ group or C₃F₇ group; k is an integer selected from the range shown in the formula; and when more than one unit exists, R₄ may differ from unit to unit.

5 [0097]

[8] The process for preparing a polyhydroxyalkanoate according to [6] or [7], characterized in that R₃ in the chemical formula (3), namely a residue having a phenyl or a thienyl structure 10 has at least any one chemical formula selected from the group consisting of chemical formulae (5), (6), (7), (8), (9), (10), (11), (12), (13), (14) and (15), wherein the chemical formula (5) is a group consisting of unsubstituted and substituted phenyl groups
15 represented by

[0098]

[Chemical Formula 73]



[0099]

20 wherein R₅ represents a substituent on the aromatic ring and is an H atom, a halogen atom, a CN group, an NO₂ group, a CH₃ group, a C₂H₅ group, a C₃H₇ group, a CH=CH₂ group, COOR₆ (R₆ represents any one of H, Na and

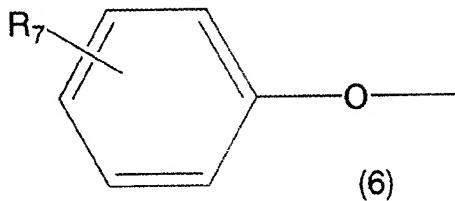
K atoms), a CF₃ group, a C₂F₅ group or a C₃F₇ group; and when more than one unit exists, R₅ may differ from unit to unit,

the chemical formula (6) is a group consisting of

5 unsubstituted and substituted phenoxy groups
represented by

[0100]

[Chemical Formula 74]



10 [0101]

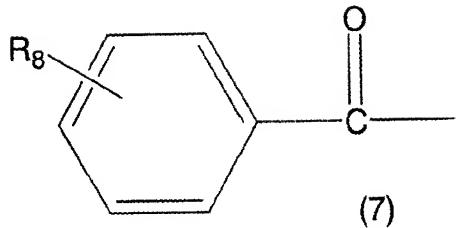
wherein R₇ represents a substituent on the aromatic ring and is an H atom, a halogen atom, a CN group, an NO₂ group, a CH₃ group, a C₂H₅ group, a C₃H₇ group, an SCH₃ group, a CF₃ group, a C₂F₅ group or a C₃F₇ group;

15 and when more than one unit exists, R₇ may differ from unit to unit,

the chemical formula (7) is a group consisting of unsubstituted and substituted benzoyl groups
represented by

20 [0102]

[Chemical Formula 75]

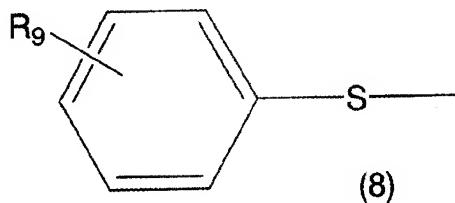


[0103]

wherein R_8 represents a substituent on the aromatic ring and is an H atom, a halogen atom, a CN group, an NO₂ group, a CH₃ group, a C₂H₅ group, a C₃H₇ group, a CF₃ group, a C₂F₅ group or a C₃F₇ group; and when more than one unit exists, R_8 may differ from unit to unit,
the chemical formula (8) is a group consisting of
unsubstituted and substituted phenylsulfanil groups
represented by

[0104]

[Chemical Formula 76]



[0105]

wherein R_9 represents a substituent on the aromatic ring and is an H atom, a halogen atom, a CN group, an NO₂ group, a COOR₁₀, an SO₂R₁₁ (R_{10} represents any one of an H atom, an Na atom, a K atom, a CH₃ group and a C₂H₅ group and R_{11} represents any one of an OH group, an ONa group, an OK group, a halogen atom, an OCH₃ group and

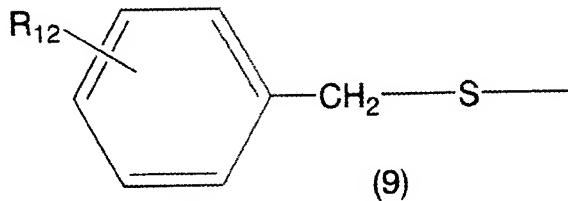
OC₂H₅ group), a CH₃ group, a C₂H₅ group, a C₃H₇ group, a (CH₃)₂-CH group or a (CH₃)₃-C group; and when more than one unit exists, R₉ may differ from unit to unit,

the chemical formula (9) is a group consisting of

5 unsubstituted and substituted (phenylmethyl)sulfanil groups represented by

[0106]

[Chemical Formula 77]



10 [0107]

wherein R₁₂ represents a substituent on the aromatic ring and is an H atom, a halogen atom, a CN group, an NO₂ group, a COOR₁₃, an SO₂R₁₄ (R₁₃ represents any one of

an H atom, an Na atom, a K atom, a CH₃ group and a C₂H₅

15 group and R₁₄ represents any one of an OH group, an ONa

group, an OK group, a halogen atom, an OCH₃ group and

OC₂H₅ group), a CH₃ group, a C₂H₅ group, a C₃H₇ group, a

(CH₃)₂-CH group or a (CH₃)₃-C group; and when more than

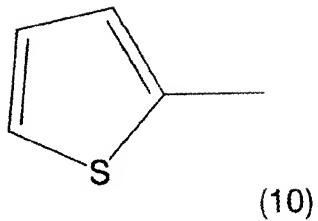
one unit exists, R₁₂ may differ from unit to unit,

20 the chemical formula (10) is 2-thienyl group

represented by

[0108]

[Chemical Formula 78]



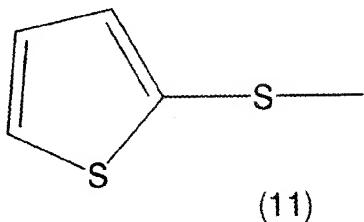
(10)

[0109]

the chemical formula (11) is 2-thienylsulfanyl group
represented by

5 [0110]

[Chemical Formula 79]



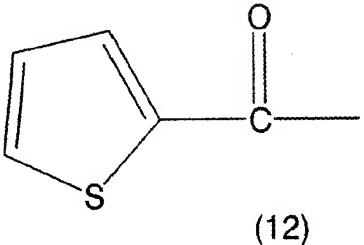
(11)

[0111]

the chemical formula (12) is a 2-thienylcarbonyl group
10 represented by

[0112]

[Chemical Formula 80]



(12)

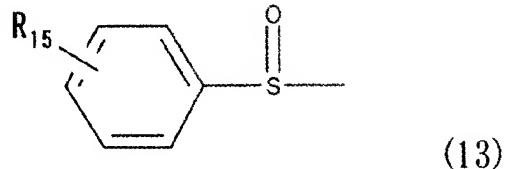
[0113]

15 the chemical formula (13) is a group consisting of

unsubstituted and substituted phenylsulfynyl groups represented by

[0114]

[Chemical Formula 81]



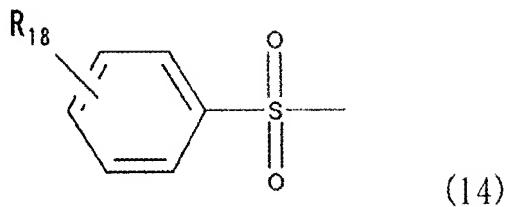
5

[0115]

wherein R_{15} represents a substituent on the aromatic ring and is an H atom, a halogen atom, a CN group, an NO_2 group, a $COOR_{16}$, an SO_2R_{17} (R_{16} represents any one of 10 an H atom, an Na atom, a K atom, a CH_3 group and a C_2H_5 group and R_{17} represents any one of an OH group, an ONa group, an OK group, a halogen atom, an OCH_3 group and OC_2H_5 group), a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $(CH_3)_2-CH$ group or a $(CH_3)_3-C$ group; and when more than 15 one unit exists, R_{15} may differ from unit to unit, the chemical formula (14) is a group consisting of unsubstituted and substituted phenylsulfonyl groups represented by

[0116]

20 [Chemical Formula 82]

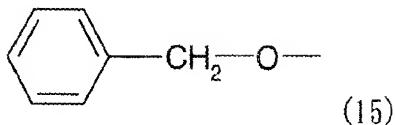


[0117]

wherein R_{18} represents a substituent on the aromatic ring and is an H atom, a halogen atom, a CN group, an NO₂ group, a COOR₁₉, an SO₂R₂₀ (R_{19} represents any one of an H atom, an Na atom, a K atom, a CH₃ group and a C₂H₅ group and R_{20} represents any one of an OH group, an ONa group, an OK group, a halogen atom, an OCH₃ group and OC₂H₅ group), a CH₃ group, a C₂H₅ group, a C₃H₇ group, a (CH₃)₂-CH group or a (CH₃)₃-C group; and when more than one unit exists, R_{18} may differ from unit to unit, and the chemical formula (15) represented by:

[0118]

[Chemical Formula 83]



15

[0119]

is a group of a (phenylmethyl)oxy group.

[0120]

[9] The process for preparing a polyhydroxyalkanoate according to any one of [6] to [8], wherein the oxidizing and cleaving step is carried out

by using one or more oxidizing agents selected from the group consisting of permanganate, bichromate and periodate.

[0121]

5 [10] The process for preparing a polyhydroxyalkanoate according to [9], wherein the oxidizing and cleaving step is carried out by using a permanganate, as an oxidizing agent, under acid conditions.

10 [0122]

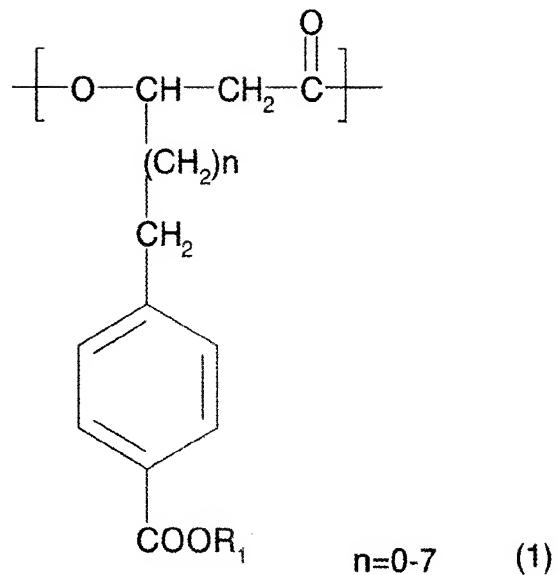
[11] The process for preparing a polyhydroxyalkanoate according to any one of [6] to [8], wherein the oxidizing and cleaving step is carried out by using ozone.

15 [0123]

[12] A charge controlling agent for controlling a charged state of powder and granular materials, the agent comprising a polyhydroxyalkanoate that has at least one kind of unit selected from the group consisting of the 3-hydroxy- ω -(4-carboxyphenyl)alkanoic acid units represented by the chemical formula (1):

[0124]

[Chemical Formula 84]



[0125]

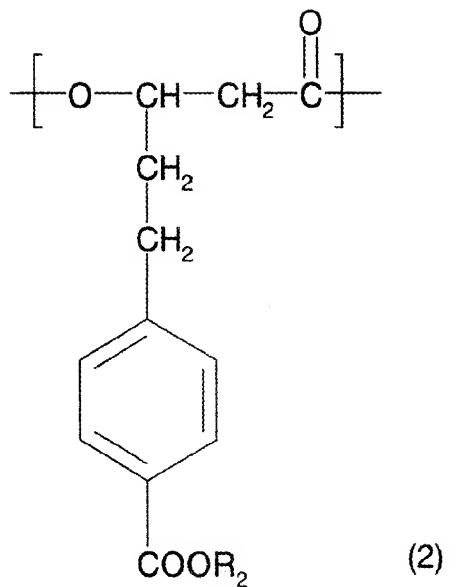
wherein n is an integer selected from the range shown
in the chemical formula; R₁ is an H, Na or K atom; and
5 when more than one unit exists, n and R₁ may differ
from unit to unit, respectively.

[0126]

[13] The charge controlling agent according to
[12], wherein the 3-hydroxy-ω-(4-
10 carboxyphenyl)alkanoic acid unit represented by the
chemical formula (1) is a 3-hydroxy-ω-(4-
carboxyphenyl)valeric acid unit represented by a
chemical formula (2):

[0126]

15 [Chemical Formula 85]



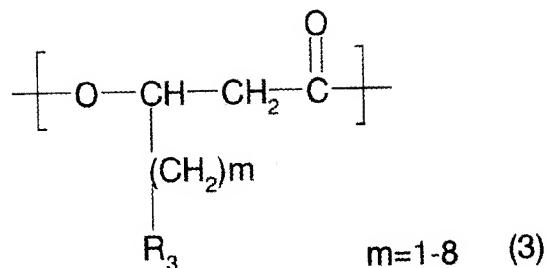
[0127]

wherein R₂ is an H, Na or K atom and, when more than one unit exists, it may differ from unit to unit.

5 [14] The charge controlling agent according to [12] or [13], comprising the polyhydroxyalkanoate which contains, in addition to the 3-hydroxy- ω -(4-carboxyphenyl)alkanoic acid unit represented by the chemical formula (1), either a 3-hydroxy- ω -substituted
10 alkanoic acid unit represented by a chemical formula (3):

[0128]

[Chemical Formula 86]

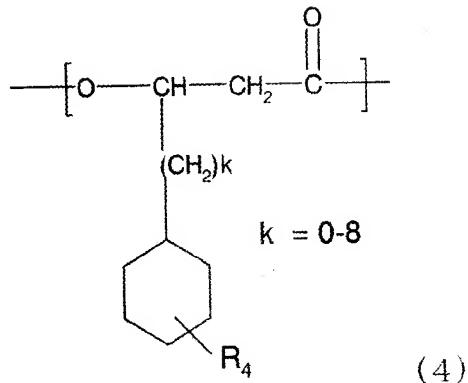


[0129]

wherein m is an integer selected from the range shown in the chemical formula; R_3 comprises a residue having
5 a ring structure of either a phenyl or a thiienyl structure; and when more than one unit exists, m and R_3 may differ from unit to unit, respectively; or

[0130]

[Chemical Formula 87]



10

[0131]

wherein R_4 represents a substituent on a cyclohexyl group and is an H atom, a CN group, an NO_2 group, a halogen atom, a CH_3 group, a C_2H_5 group, a C_3H_7 group, a
15 CF_3 group, a C_2F_5 group or a C_3F_7 group; k is an integer

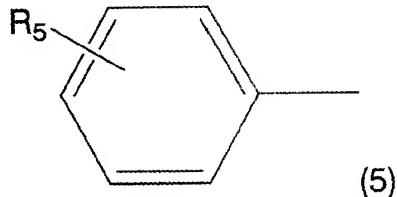
selected from 0 to 8; and when more than one unit exists, k and R₄ may differ from unit to unit.

[0132]

[15] The charge controlling agent according to
5 any one of [12] to [14], comprising the polyhydroxyalkanoate wherein R₃ in the chemical formula (3) having a phenyl or thienyl structure is at least any one selected from the group consisting of residues represented by chemical formula (5), (6), (7), (8),
10 (9), (10), (11), (12), (13), (14) and (15), wherein the chemical formula (5) represents a group consisting of unsubstituted and substituted phenyl groups:

[0133]

15 [Chemical Formula 88]



[0134]

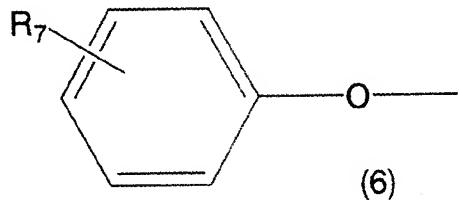
wherein R₅ represents a substituent on the aromatic ring and is an H atom, a halogen atom, a CN group, an NO₂ group, a CH₃ group, a C₂H₅ group, a C₃H₇ group, a CH=CH₂ group, COOR₆ (R₆ represents any one of H, Na and K atoms), a CF₃ group, a C₂F₅ group or a C₃F₇ group; and when more than one unit exists, R₅ may differ from unit

to unit;

the chemical formula (6) represents a group consisting of unsubstituted and substituted phenoxy groups:

[0135]

5 [Chemical Formula 89]



(6)

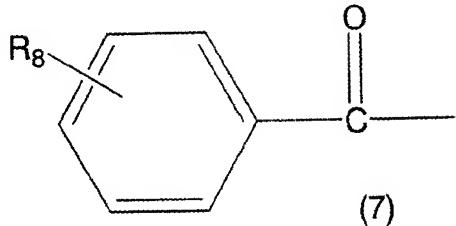
[0136]

wherein R_7 represents a substituent on the aromatic ring and is an H atom, a halogen atom, a CN group, an 10 NO_2 group, a CH_3 group, a C_2H_5 group, a C_3H_7 group, an SCH_3 group, a CF_3 group, a C_2F_5 group or a C_3F_7 group; and when more than one unit exists, R_7 may differ from unit to unit;

the chemical formula (7) represents a group consisting 15 of unsubstituted and substituted benzoyl groups:

[0137]

[Chemical Formula 90]



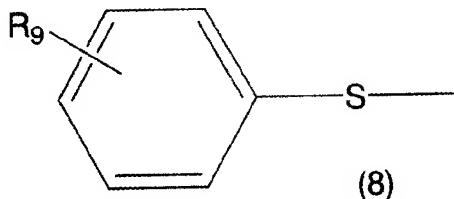
(7)

[0138]

wherein R_8 represents a substituent on the aromatic ring and is an H atom, a halogen atom, a CN group, an NO_2 group, a CH_3 group, a C_2H_5 group, a C_3H_7 group, a CF_3 group, a C_2F_5 group or a C_3F_7 group; and when more than 5 one unit exists, R_8 may differ from unit to unit; the chemical formula (8) represents a group consisting of unsubstituted and substituted phenylsulfanil groups:

[0139]

[Chemical Formula 91]



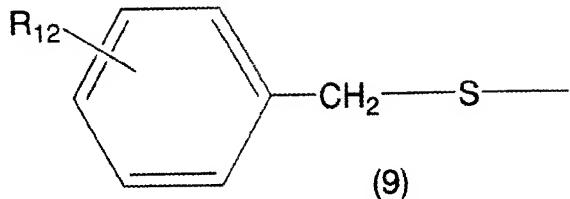
10

[0140]

wherein R_9 represents a substituent on the aromatic ring and is an H atom, a halogen atom, a CN group, an NO_2 group, a $COOR_{10}$, an SO_2R_{11} (R_{10} represents any one of 15 an H atom, an Na atom, a K atom, a CH_3 group and a C_2H_5 group and R_{11} represents any one of an OH group, an ONa group, an OK group, a halogen atom, an OCH_3 group and OC_2H_5 group), a CH_3 group, a C_2H_5 group, a C_3H_7 group, a $(CH_3)_2-CH$ group or a $(CH_3)_3-C$ group; and when more than 20 one unit exists, R_9 may differ from unit to unit; the chemical formula (9) represents a group consisting of unsubstituted and substituted (phenylmethyl)sulfanil groups:

[0141]

[Chemical Formula 92]

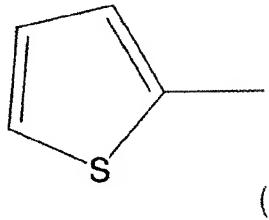


[0142]

wherein R_{12} represents a substituent on the aromatic
5 ring and is an H atom, a halogen atom, a CN group, an
NO₂ group, a COOR₁₃, an SO₂R₁₄ (R_{13} represents any one of
an H atom, an Na atom, a K atom, a CH₃ group and a C₂H₅
group and R_{14} represents any one of an OH group, an ONa
group, an OK group, a halogen atom, an OCH₃ group and
10 OC₂H₅ group), a CH₃ group, a C₂H₅ group, a C₃H₇ group, a
(CH₃)₂-CH group or a (CH₃)₃-C group; and when more than
one unit exists, R_{12} may differ from unit to unit;
the chemical formula (10) represents 2-thienyl group:

[0143]

15 [Chemical Formula 93]



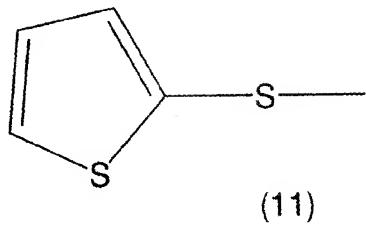
;

[0144]

the chemical formula (11) represents a 2-
thienylsulfanil group:

20 [0145]

[Chemical Formula 94]



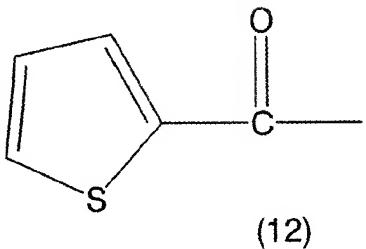
;

[0146]

the chemical formula (12) represents a 2-thienylcarbonyl group:
5

[0147]

[Chemical Formula 95]



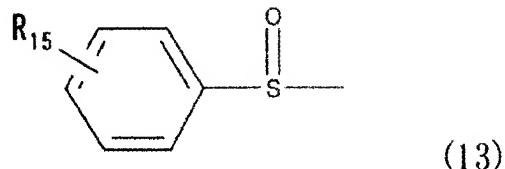
;

[0148]

10 the chemical formula (13) represents a group consisting
of unsubstituted and substituted phenylsulfenyl groups:

[0149]

[Chemical Formula 96]



15 [0150]

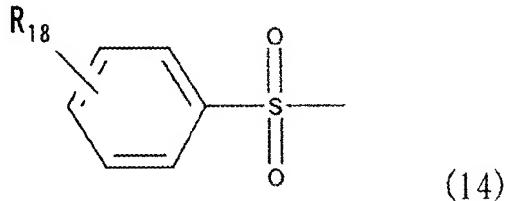
wherein R₁₅ represents a substituent on the aromatic

ring and is an H atom, a halogen atom, a CN group, an NO₂ group, a COOR₁₆, an SO₂R₁₇ (R₁₆ represents any one of an H atom, an Na atom, a K atom, a CH₃ group and a C₂H₅ group and R₁₇ represents any one of an OH group, an ONa group, an OK group, a halogen atom, an OCH₃ group and OC₂H₅ group), a CH₃ group, a C₂H₅ group, a C₃H₇ group, a (CH₃)₂-CH group or a (CH₃)₃-C group; and when more than one unit exists, R₁₅ may differ from unit to unit;

5 the chemical formula (14) represents a group consisting of unsubstituted and substituted phenylsulfonyl groups:

10 [0151]

[Chemical Formula 97]



[0152]

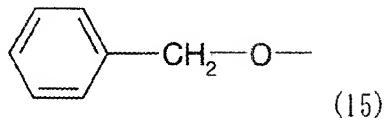
15 wherein R₁₈ represents a substituent on the aromatic ring and is an H atom, a halogen atom, a CN group, an NO₂ group, a COOR₁₉, an SO₂R₂₀ (R₁₉ represents any one of an H atom, an Na atom, a K atom, a CH₃ group and a C₂H₅ group and R₂₀ represents any one of an OH group, an ONa group, an OK group, a halogen atom, an OCH₃ group and OC₂H₅ group), a CH₃ group, a C₂H₅ group, a C₃H₇ group, a (CH₃)₂-CH group or a (CH₃)₃-C group; and when more than one unit exists, R₁₈ may differ from unit to unit; and

20

the chemical formula (15):

[0153]

[Chemical Formula 98]



5 [0154]

represents a group of a (phenylmethyl)oxy group.

[0155]

[16] The charge controlling agent according to
any one of [12] to [15], wherein the powder and
10 granular material is a toner for developing
electrostatic latent images.

[0156]

[17] The charge controlling agent according to
any one of [12] to [16], wherein a number average
15 molecular weight of the polyhydroxyalkanoate is
selected to fall in a range of 1000 to 1000000.

[0157]

[18] A toner binder to be used in a toner for
developing an electrostatic latent image, containing
20 the charge controlling agent according to any one of
[12] to [17].

[0158]

[19] A toner for developing an electrostatic
latent image comprising at least a binder resin, a
25 colorant and a charge controlling agent according to

any one of [12] to [17].

[0159]

[20] An image forming method comprising at least the steps of

5 charging an electrostatic latent image-holding member by applying voltage to a charging member from outside;

 forming an electrostatic latent image on the charged electrostatic latent image-holding member;

10 developing the electrostatic latent image with a toner for developing electrostatic latent images to form a toner image on the electrostatic latent image-holding member;

 transferring the toner image on the electrostatic 15 latent image-holding member to a recording medium; and fixing the toner image on the recording medium by heat,

 wherein the toner for developing an electrostatic latent image comprising at least a binder resin, a colorant and the charge controlling agent according to 20 any one of [12] to [17] is used.

[0160]

[21] The image forming method according to [20], comprising at least

25 the step of charging an electrostatic latent image-holding member by applying voltage to a charging member from outside;

 the step of forming an electrostatic latent image

on the charged electrostatic latent image-holding member;

the step of developing the electrostatic latent image with a toner for developing electrostatic latent

5 images to form a toner image on the electrostatic latent image-holding member;

a first transferring step of transferring the toner image on the electrostatic latent image-holding member to an intermediate transfer medium;

10 a second transferring step of transferring the toner image on the intermediate transfer medium to the recording medium; and

fixing the toner image on the recording medium by heat,

15 wherein the toner for developing an electrostatic latent image comprising at least a binder resin, a colorant and the charge controlling agent according to any one of [12] to [17] is used.

[0161]

20 [22] An image forming apparatus comprising at least charging means for charging an electrostatic latent image-holding member by applying voltage to a charging member from outside; electrostatic latent image forming means for forming an electrostatic latent 25 image on the charged electrostatic latent image-holding member; developing means for developing the electrostatic charge image with a toner for developing

electrostatic charge images to form a toner image on
the electrostatic latent image-holding member;
transferring means for transferring the toner image on
the electrostatic latent image-holding member to a
5 recording medium; and fixing means for fixing the toner
image on the recording medium by heat, wherein the
toner for developing an electrostatic latent image
comprising at least a binder resin, a colorant and the
charge controlling agent according to any one of [12]
10 to [17] is used.

[0162]

[23] The image forming apparatus according to
[22], comprising at least charging means for charging
an electrostatic latent image-holding member by
15 applying voltage to a charging member from outside;
electrostatic latent image forming means for forming an
electrostatic latent image on the charged electrostatic
latent image-holding member; developing means for
developing the electrostatic charge image with a toner
20 for developing electrostatic charge images to form a
toner image on the electrostatic latent image-holding
member; a first transferring means for transferring the
toner image on the electrostatic latent image-holding
member to an intermediate transfer medium; a second
25 transferring means for transferring the toner image on
the intermediate transfer medium to the recording
medium; and fixing means for fixing the toner image on

the recording medium by heat, wherein the toner for developing an electrostatic latent image comprising at least a binder resin, a colorant and the charge controlling agent according to any one of [12] to [17]
5 is used.

[0163]

Hereinafter the contents of the present invention will be described in details.

[0164]

10 [Embodiment(s)]

Polyhydroxyalkanoates used in this invention each have a fundamental skeleton as a biodegradable resin; therefore, they have outstanding characteristics in that they are melt-fablicable and can be utilized in
15 the production of various articles, like conventional plastics, and at the same time, they are degraded by organisms and taken in the natural cycle of matter, unlike synthesized polymers derived from petroleum. As a result, they can be disposed without burning
20 treatment, which means they are useful materials even from a viewpoint of prevention of air pollution and global warming and can be utilized as plastics that serve for the conservation of the environment.

[0165]

25 The polyhydroxyalkanoates including a unit represented by the chemical formula (1), which this invention aims at, are produced by biosynthesizing, as

a starting material, a 3-hydroxy- ω -(4-vinylphenyl)alkanoic acid unit of the chemical formula (16), which includes a carbon-carbon double bond at the end of its side chain.

5 [0166]

The polyhydroxyalkanoates including a unit represented by the chemical formula (16), which are used as a starting material for this invention, can be prepared by, not limited to, the methods such as a 10 microbial production process; a plant system in which genes are manipulated; and chemical polymerization. Preferably, the microbial production process is used.

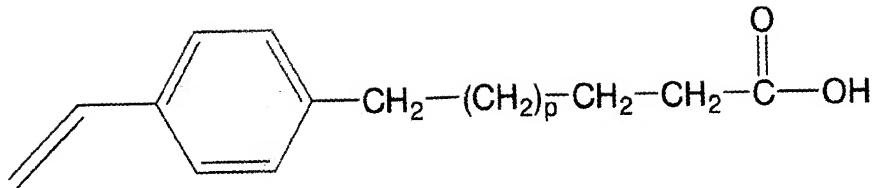
[0167]

A method of preparing a polyhydroxyalkanoate 15 including a unit represented by the chemical formula (16), as a starting material, will be described.

The above polyhydroxyalkanoate as a starting material is prepared by the method characterized by culturing the above described microorganism in a medium 20 that contains at least one kind of alkanoic acid selected from the group consisting of ω -(4-vinylphenyl)alkanoic acid represented by the chemical formula (17).

[0168]

25 [Chemical Formula 99]



p=0.7 (17)

[0169]

wherein p is an integer selected from the range shown in the chemical formula.

5 The microorganism for use in the method of producing polyhydroxyalkanoate containing units each expressed by chemical formula (16) as a starting material according to the present invention may be any microorganism as long as it is a microorganism capable
10 of producing a PHA type polyester containing ω -3-hydroxy- ω -(4-vinylphenyl) alkanoic acid units expressed by general chemical formula (16) by culturing the microorganism in a culture medium containing ω -(4-vinylphenyl) alkanoic acid expressed by general
15 chemical formula (17). A suitable example of usable microorganisms capable of producing PHA may be a microorganism belonging to genus Pseudomonas. Above all, more preferable are strains which are capable of producing PHA, while having no enzyme reactivity to
20 oxidize or epoxidized the vinyl group existing as a substituent on the phenyl group.

[0170]

More specifically, among microorganisms belonging to *Pseudomonas*, more preferable species as the microorganism for use in the production method of the present invention may include *Pseudomonas cichorii*,
5 *Pseudomonas putida*, *Pseudomonas fluorescens*,
Pseudomonas oleovolans, *Pseudomonas aeruginosa*,
Pseudomonas stutzeri, and *Pseudomonas jessenii*.

[0171]

Further, a more suitable strain includes, for
10 example, *Pseudomonas cichorii* YN2 (FERM BP-7375),
Pseudomonas cichorii H45 (FERM BP-7374), *Pseudomonas*
jessenii P161 (FERM BP-7376) and *Pseudomonas putida* P91
(FERM BP-7373). These four types of strains are
deposited on November 20, 2000 at International Patent
15 Organism Depository, National Institute of Advanced
Industrial Science and Technology (independent
administrative corporation), AIST Tsukuba Central 6, 1-
1, Higashi 1-chome, Tsukuba-shi, Ibaraki-ken 305-8566
Japan, and described in Japanese Patent Application
20 Laid-Open No. 2001-288256 (Patent Document 28).

[0172]

These microorganisms are capable of producing
polyhydroxyalkanoate containing a corresponding ω -
substituted-3-hydroxy-alkanoic acid as a monomer unit
25 using as a raw material a ω -substituted-straight chain
alkanoic acid substituted at the chain terminal with a
six-membered ring atom group such as a substituted or

unsubstituted phenyl group, a substituted or
unsubstituted phenoxy group and a substituted or
unsubstituted cyclohexyl group, or a ω -substituted-
straight chain alkanoic acid substituted at the chain
5 terminal with a five-membered ring atom group such as a
thienyl group.

[0173]

In the production method of the present invention,
any culture medium may be used in the process of
10 culturing a microorganism as long as it is an inorganic
salt culture medium containing a phosphate and a
nitrogen source such as an ammonium salt or nitrate.
In the process of producing PHA in the microorganism,
the productivity of PHA may be improved by adjusting
15 the concentration of the nitrogen source.

[0174]

In addition, nutrients such as an yeast extract,
polypeptone and meat extract can be added to the
culture medium as a substrate for promoting the
20 propagation of the microorganism. That is, peptides
may be added as an energy source and a carbon source in
the form of nutrients such as an yeast extract,
polypeptone and a meat extract.

[0175]

25 Alternatively, the culture medium may contain
saccharides, for example, aldoses such as
glyceroaldehyde, erythrose, arabinose, xylose, glucose,

galactose, mannose and fructose, alditols such as glycerol, erythritol and xylitol, aldonic acids such as gluconic acid, uronic acids such as glucuronic acid and galacturonic acid, and disaccharides such as maltose,

5 sucrose and lactose as an energy source and carbon source consumed for propagation of the microorganism.

[0176]

Instead of the above described saccharides, organic acids or salts thereof, more specifically 10 organic acids involved in the TCA cycle and organic acids derived from the TCA cycle by a biochemical reaction of a few steps, or water soluble salts thereof may be used. As the organic acid or salt thereof, hydroxycarboxylic acids and oxocarboxylic acids such as 15 pyruvic acid, oxalacetic acid, citric acid, isocitric acid, ketoglutaric acid, succinic acid, fumaric acid, malic acid and lactic acid or water soluble salts thereof can be used. Alternatively, amino acids or salts thereof, for example amino acids such as 20 aspartic acid and glutamic acid or salts thereof can be used. When the organic acid or salt thereof is added, it is more preferable that one or more types are selected from a group consisting of pyruvic acid, oxalacetic acid, citric acid, isocitric acid, 25 ketoglutaric acid, succinic acid, fumaric acid, malic acid, lactic acid and salts thereof, and added to the culture medium and dissolved therein. Alternatively,

when the amino acid or salt thereof is added, it is more preferable that one or more types are selected from a group consisting of asparaginic acid, glutamic acid and salts thereof, and added to the culture medium 5 and dissolved therein. At this time, as required, all or part thereof can be added in the form of a water soluble salt to be dissolved uniformly without affecting the pH of the culture medium.

[0177]

10 It is desirable that the concentration of the above coexisting substrate added to the culture medium as a carbon source for growth of the microorganism and energy source for production of polyhydroxyalkanoate is usually selected so that it is in the range of from 0.1 15 to 5% (w/v), more preferably 0.2 to 2% (w/v) per culture medium. That is, for peptides, yeast extracts, organic acids or salts thereof, amino acids or salts thereof, and saccharides, which are used as the above coexisting substrates, one or more types thereof may be 20 added, and, it is desirable that the total concentration of these added substrates is within the above described range of total concentrations.

[0178]

As substrates for producing an intended 25 polyhydroxyalkanoate, namely, the content of ω -(4-vinylphenyl)alkanoic acid represented by the chemical formula (17) is selected to fall in the range of 0.01%

to 1% (w/v) per medium and more preferably in the range of 0.02% to 0.2% (w/v).

[0179]

Any temperature at which microorganism strains to
5 be used can suitably be propagated may be selected as a culture temperature, and an appropriate temperature is usually in the range of from about 15 to 37°C, more preferably from about 20 to 30°C.

[0180]

10 Any culture method such as liquid culture and solid culture may be used for the culture as long as it allows propagation of microorganism and production of PHA. In addition, any type of culture method such as batch culture, fed-batch culture, semi-continuous
15 culture and continuous culture may be used. Forms of liquid batch culture include a method of supplying oxygen by shaking the microorganism in a shaking flask, and a method of supplying oxygen by aeration-agitation using a jar fermenter.

20 [0181]

For the method of making the microorganism produce and accumulate PHA, a two-step culture method in which the microorganism is cultured by two steps may be adopted other than the one-step culture method in which
25 the microorganism is cultured in an inorganic salt culture medium containing a phosphate and a nitrogen source such as an ammonium salt or a nitrate with the

substrate added therein in a predetermined concentration as described above. In this two-step culture method, the microorganism is once propagated sufficiently in the inorganic salt culture medium

5 containing a phosphate and a nitrogen source such as an ammonium salt or a nitrate with a substrate added therein in a predetermined concentration as a primary culture, and thereafter cells obtained by the primary culture are transferred to a culture medium containing

10 the substrate in a predetermined concentration where the amount of nitrogen source such as ammonium chloride is limited, and are further cultured as a secondary culture, thereby making the microorganism produce and accumulate PHA. Use of this two-step culture method

15 may improve the productivity of desired PHA.

[0182]

Generally, a produced PHA type polyester has reduced water solubility because of the presence of hydrophobic atomic groups such as a 4-vinylphenyl group

20 of a 3-hydroxy- ω -(4-vinylphenyl)alkanoic acid unit in the side chain, and is accumulated in cells producing PHA, and can easily be separated from the culture medium by culturing cells and collecting the cells producing and accumulating the desired PHA type

25 polyester. After the collected cells are washed and dried, the desired PHA type polyester can be collected.

[0183]

In addition, polyhydroxyalkanoate is usually accumulated in cells of such a microorganism capable of producing PHA. For the method of collecting desired PHA from these microorganism cells, a method that is 5 usually used may be adopted. For example, extraction with an organic solvent such as chloroform, dichloromethane and acetone is most convenient. Other than the above described solvents, dioxane, tetrahydrofuran and acetonitrile may be used. In 10 addition, in a working environment in which use of any organic solvent is not preferred, a method in which instead of solvent extraction, any one of a treatment by surfactants such as SDS, a treatment by enzymes such as lysozyme, a treatment by chemicals such as 15 hypochlorites, ammonium and EDTA, an ultrasonic disruption method, a homogenizer method, a pressure disruption method, a bead impulse method, a grinding method, a pounding method and a freeze-thaw method is used to physically disrupt microorganism cells, 20 followed by removing cell components other than PHA to collect PHA may be adopted.

[0184]

As an example of inorganic salt media applicable to the production method of this invention, the 25 composition of an inorganic salt medium (M9 medium), which is used in the examples described later, is shown below.

[0185]

(Composition of M9 culture medium)

Na₂HPO₄: 6.3

KH₂PO₄: 3.0

5 NH₄Cl: 1.0

NaCl: 0.5

(by g/L, pH=7.0).

Further, for ensuring satisfactory propagation of cells and associated improvement of productivity of 10 PHA, essential trace elements such as essential trace metal elements should be added in an appropriate amount to an inorganic salt culture medium such as the above described M9 culture medium, and it is very effective to add a solution of trace components to about 0.3% 15 (v/v), of which composition is shown below. The addition of such a trace component solution supplies trace metal elements for use in propagation of the microorganism.

[0186]

20 (Composition of trace component solution)

nitrilotriacetic acid: 1.5;

MgSO₄: 3.0; MnSO₄: 0.5; NaCl: 1.0;

FeSO₄: 0.1; CaCl₂: 0.1; CoCl₂: 0.1;

ZnSO₄: 0.1; CuSO₄: 0.1; AlK(SO₄)₂: 0.1;

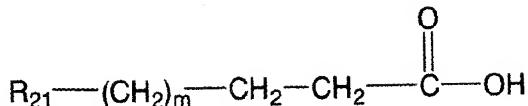
25 H₃BO₃: 0.1; Na₂MoO₄: 0.1; NiCl₂: 0.1 (g/L).

Furthermore, if at least one kind of monomer unit of ω -substituted alkanoic acid compound represented by

the chemical formula (18) or at least one kind of monomer unit of ω -cyclohexyl alkanoic acid compound represented by the chemical formula (19) is allowed to coexist with a substrate for producing an intended 5 polyhydroxyalkanoate, that is, at least one kind of monomer unit selected from the group consisting of ω -(4-vinylphenyl) alkanoic acid represented by the chemical formula (17) during the culture, a polyhydroxyalkanoate can be produced which includes a 10 3-hydroxy- ω -substituted alkanoic acid unit represented by the chemical formula (3) or a 3-hydroxy- ω -cyclohexyl alkanoic acid unit represented by the chemical formula (4), besides a 3-hydroxy- ω -(4-vinylphenyl)alkanoic acid unit represented by the 15 chemical formula (16). In this case, the contents of at least one monomer unit selected from the group consisting of ω -(4-vinylphenyl) alkanoic acid represented by the chemical formula (17), at least one kind of monomer unit of ω -substituted alkanoic acid 20 compound represented by the chemical formula (18), and at least one kind of monomer unit of ω -cyclohexyl alkanoic acid compound represented by the chemical formula (19) are preferably selected to each fall in the range of 0.01% to 1% (w/v) per medium and more 25 preferably in the range of 0.02% to 0.2% (w/v) per medium:

[0187]

[Chemical Formula 100]



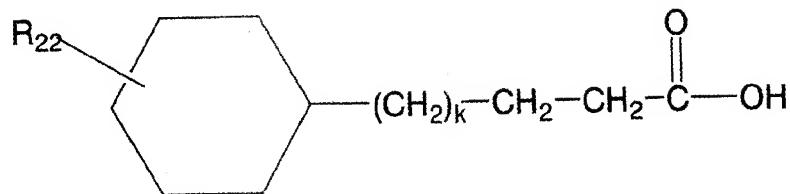
$m=1-8 \quad (18)$

[0188]

wherein m is an integer selected from the range shown
5 in the formula; R_{21} includes a ring structure of a
phenyl or thienyl structure and has any one chemical
formula selected from the group consisting of the above
described chemical formulae (8), (9), (10), (11), (12),
(13), (14), (15), (16), (17); and when more than one
10 unit exists, may differ from unit to unit:

[0189]

[Chemical Formula 101]



$k=0-8 \quad (19)$

[0190]

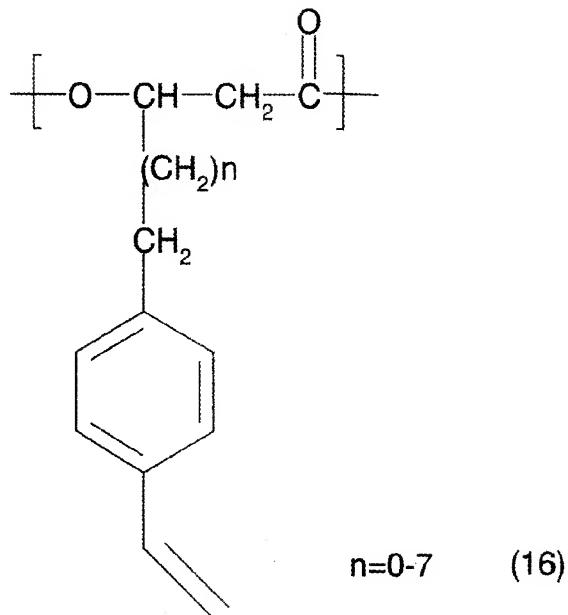
15 wherein R_{22} represents a substituent on the cyclohexyl
group and is an H atom, a CN group, an NO_2 group, a
halogen atom, a CH_3 group, a C_2H_5 group, C_3H_7 group, CF_3
group, C_2F_5 group or a C_3F_7 group; k is an integer

selected from the range shown in the formula.

Polyhydroxyalkanoates represented by the chemical formula (1), which this invention aims at, are produced by using, as starting materials, polyhydroxyalkanoates 5 that include 3-hydroxy- ω -(4-vinylphenyl)alkanoic acid unit represented by the chemical formula (16) and oxidizing and cleaving the double bond portion. In the above oxidation and cleavage reaction of this invention, when R₃ of the units represented by the 10 chemical formula (3) is a residue represented by the chemical formula (8), the sulfide bond of the residue may sometimes be oxidized into a sulfoxide or a sulfon.

[0191]

[Chemical Formula 102]



15

[0192]

wherein n is an integer selected from 0 to 7; and when more than one unit exists, n may differ from unit to unit.

Examples of known methods of oxidizing and
5 cleaving a carbon-carbon double bond into carboxylic acid using an oxidizing agent are: a method using permanganate (J. Chem. Soc., Perkin. Trans. 1, 806 (1973); (Non-patent Document 11)), a method using bichromate (Org. Synth., 4, 698 (1963); (Non-patent
10 Document 12)), a method using periodate (J. Org. Chem., 46, 19 (1981); Non-patent Document 13)), a method using a nitrate (Japanese Patent Application Laid-Open No. S59-190945; (Patent Document 29), and a method using ozone (J. Am. Chem. Soc., 81, 4273 (1959); (Non-patent
15 Document 14)). And as to polyhydroxyalkanoates, a method is reported in the above-mentioned Macromolecular chemistry, 4, 289-293 (2001) (Non-patent Document 10) in which the carbon-carbon double bond at the end of polyhydroxyalkanoate side chain is oxidized
20 under acid conditions using potassium permanganate as an oxidizing agent, to obtain carboxylic acid. In this invention, the same method can be used.

[0193]

Preferred oxidizing agents used in this invention
25 are, not limited to, permanganates. Of permanganates, potassium permanganate is generally used as an oxidizing agent. The amount of permanganate used

should be usually 1 mol equivalent or more per mol of unit represented by the chemical formula (16) and preferably 2 to 10 mol equivalent, since oxidation and cleavage reaction proceeds stoichiometrically.

5 [0194]

To allow a reaction system to be under acid conditions, various inorganic acids and organic acids, such as sulfuric acid, hydrochloric acid, acetic acid and nitric acid, are usually used. However, when using 10 an acid such as sulfuric acid, nitric acid or hydrochloric acid, the ester bond of the polyhydroxyalkanoate backbone chain might be broken, causing decrease in molecular weight. Accordingly, acetic acid is preferably used. The amount of acid 15 used is usually in the range of 0.2 to 200 mol equivalent per mol of unit represented by the chemical formula (16) and preferably in the range of 0.4 to 100 mol equivalent. The amount less than 0.2 mol equivalent gives the carboxyl acid in a low yield, whereas the amount more than 200 mol equivalent gives 20 the degradation products, as by-product, by the acid; therefore neither case are preferable. In order to accelerate the reaction, crown ether can also be used. In this case, crown ether and permanganate form a 25 complex, which increases the reactivity. As the crown ether, dibenzo-18-crown-6-ether, dicyclo-18-crown-6-ether or 18-crown-6-ether is generally used. The

amount of crown ether used is usually in the range of 0.5 to 2.0 mol equivalent per mol of permanganate and preferably in the range of 0.5 to 2.0 mol equivalent.

[0195]

5 As a solvent used in the oxidation and cleavage reaction of this invention, any solvents can be used as long as they are inactive in the oxidation reaction. For example, water; acetone; ethers such as tetrahydrofuran and dioxane; aromatic hydrocarbons such 10 as benzene, toluene and xylene; aliphatic hydrocarbons such as hexane and heptane; and hydrocarbon halides such as methyl chloride, dichloromethane and chloroform can be used. Of these solvents, hydrocarbon halides, such as methyl chloride, dichloromethane and chloroform 15 are preferable, taking into consideration the solubility of polyhydroxyalkanoates.

[0196]

 In the above described oxidation and cleavage reaction, a polyhydroxyalkanoate including a unit 20 represented by the chemical formula (16), a permanganate and an acid may be introduced into a solvent at a time from the beginning and reacted together, or they may be added to the reaction system one by one continuously or intermittently to be 25 reacted. Or first a permanganate alone is dissolved or suspended in a solvent, followed by continuous or intermittent addition of a polyhydroxyalkanoate and an

acid to the reaction system, or first a polyhydroxyalkanoate alone is dissolved or suspended in a solvent, followed by continuous or intermittent addition of a permanganate and an acid to the reaction
5 system. Further, first a polyhydroxyalkanoate and an acid are introduced into a solvent and then a permanganate is added to the reaction system continuously or intermittently to be reacted, or first permanganate and an acid are introduced into a solvent
10 and then polyhydroxyalkanoate is added to the reaction system continuously or intermittently, or first a polyhydroxyalkanoate and a permanganate are introduced into a solvent and then an acid is added to the reaction system continuously and intermittently to be
15 reacted.

[0197]

The reaction temperature should be usually -40 to 40°C and preferably -10 to 30°C. The reaction time should be usually 2 to 48 hours, though it depends on
20 the stoichiometric ratio of the unit represented by the chemical formula (16) to the permanganate and the reaction temperature.

[0198]

When using a polyhydroxyalkanoate that includes a
25 3-hydroxy- ω -substituted alcanoic acid unit represented by the chemical formula (3) or a 3-hydroxy- ω -cyclohexyl alcanoic acid unit represented by the

chemical formula (4), besides a 3-hydroxy- ω -(4-vinylphenyl)alkanoic acid unit represented by the chemical formula (16), the reaction can be conducted under the same conditions.

5 [0199]

In addition, this invention provides a charge controlling agent, and in addition, a toner for developing electrostatic charge images that contains the charge controlling agent. Furthermore, this 10 invention is an image forming method including a charging step of charging an electrostatic latent image-holding member uniformly by applying voltage to a charging member from the outside; a developing step of forming a toner image on the electrostatic latent 15 image-holding member; a transferring step of transferring the toner image on the electrostatic latent image-holding member to a transfer medium through or not through an intermediate transfer medium; and a heat fixing step of fixing the toner image on the 20 transfer medium by heat. Further, this invention is an image forming apparatus including means corresponding to the steps of the above image forming method, that is, charging means, developing means, transferring means and heat fixing means.

25 [0200]

What is important in the structure of polyhydroxyalkanoates used in this invention is that it

includes a carboxyphenyl structure on its side chain, i.e., it has an aromatic ring substituted with on the side chain, just like the monomer units represented by the chemical formula (1). The units having an anionic or electron attractive group are preferable to further improve the negative chargeability of charge controlling agents; in actuality, the charge controlling agent of this invention has superior negative chargeability.

10 [0201]

Polyhydroxyalkanoate used in the present invention has good compatibility with the binder resin and excellent compatibility particularly with polyester type binder resin. The toner containing 15 polyhydroxyalkanoate according to the present invention has a high specific charge level and is excellent in stability with time to provide clear images stably in electrostatic recording even after being stored for a long time period. PHA of the invention can be used for 20 both black and color toners of negative chargeability because of its colorlessness and negative-electrifiability.

[0202]

In addition, by properly selecting the type and 25 composition ratio of monomer units constituting polyhydroxyalkanoate according to the present invention, wide range compatibility control is

possible. If a resin composition is selected such that the charge controlling agent is in micro-phase separation state in a toner binder, no electric continuity is formed in the toner so that electric 5 charge can stably be maintained. In addition, polyhydroxyalkanoate according to the present invention contains no heavy metals, and therefore when the toner is produced by suspension polymerization or emulsion polymerization, polymerization inhibition due to the 10 presence of heavy metals, as found with a metal-containing charge controlling agent, does not occur, thus making it possible to produce a toner with stability.

[0203]

15 <Addition of PHA to toner>

In the present invention, PHA can be added to a toner by a method of internal addition to the toner or a method of external addition to the toner. The addition amount of the internal addition is generally 20 0.1 to 50% by weight, preferably 0.3 to 30% by weight, and further preferably 0.5 to 20% by weight as the weight ratio of the toner binder and the charge controlling agent. If it is lower than 0.1% by weight, the improvement degree of the charging property of the 25 toner is insignificant and thus not preferable.

Whereas, if it is higher than 50% by weight, it is not preferably from an economical point of view. Further,

in the case of the external addition, the weight ratio of the toner binder and the charge controlling agent is preferably 0.01 to 5% by weight, and it is particularly preferable that the compound is mechanochemically fixed
5 on the surface of the toner. In addition, polyhydroxyalkanoate according to the present invention may be used in combination with a known charge controlling agent.

[0204]

10 The number average molecular weight of polyhydroxyalkanoate according to the present invention is usually 1000 to 1000000, preferably 1000 to 300000. If it is less than 1000, the compound is completely compatible with the toner binder to make it difficult
15 to form a discontinuous domain, resulting in an insufficient charge level, and the fluidity of the toner is adversely affected. Further, if it is higher than 1000000, dispersion in the toner becomes difficult.

20 [0205]

The molecular weight of polyhydroxyalkanoate according to the present invention was measured by GPC (gel permeation chromatography). For the specific method of measurement by GPC, a sample was prepared by
25 dissolving the above polyhydroxyalkanoate in chloroform or dimethylformamide (DMF) containing 0.1% by weight of LiBr. Using a similar mobile phase, the molecular-

weight distribution was determined from a calibration curve of standard polystyrene resin.

[0206]

In addition, in the present invention, the above 5 polyhydroxyalkanoate with the ratio (M_w/M_n) of the weight average molecular weight (M_w) to the number average molecular weight (M_n) measured as described above being in the range of from 1 to 10 are preferably used.

10 [0207]

Polyhydroxyalkanoate to be used in the present invention has a melting point preferably in the range of from 20 to 150°C, especially preferably from 40 to 150°C, or has no melting point but a glass transition 15 temperature in the range of from 20 to 150°C, especially preferably from 40 to 150°C. If the foregoing melting point is lower than 20°C or the glass transition temperature with no melting point is lower than 20°C, the fluidity and the storage property of the 20 toner are often adversely affected. Whereas if the foregoing melting point is higher than 150°C or the glass transition temperature with no melting point is higher than 150°C, the charge controlling agent becomes difficult to be kneaded with the toner and the charge 25 level distribution becomes broad in many cases.

[0208]

To measure the melting point T_m and the glass

transition temperature Tg in this case, a high precision and internally heating input compensation type differential scanning calorimeter, for example, DSC-7 manufactured by Perkin Elmer Co., may be
5 employed.

[0209]

Regarding the toner binder and the toner of the present invention, the weight ratio of the toner binder and the charge controlling agent is generally 0.1 to
10 50% by weight, preferably 0.3 to 30% by weight, and more preferably 0.5 to 20% by weight. Regarding the composition ratio of the toner of the present invention, generally the foregoing charge controlling agent is in the range of from 0.1 to 50% by weight, the
15 toner binder is in the range of from 20 to 95% by weight, and a coloring material is in the range of from 0 to 15% by weight with respect to the weight of the toner and based on the necessity, a magnetic powder (a powder of a ferromagnetic metal such as iron, cobalt,
20 nickel and the like and a compound such as magnetite, hematite, ferrite and the like) functioning as a coloring material may be added in an amount not more than 60% by weight. Further, various additives such as a lubricant (polytetrafluoroethylene, a lower molecular
25 weight polyolefin, an aliphatic acid or its metal salt or amide, and the like) and other charge controlling agents (metal-containing azo dye, metal salicylate,

etc.) may be contained. In addition, in order to improve the fluidity of the toner, a hydrophobic colloidal silica fine powder may also be employed. The amounts of these additives are generally not more than 5 10% by weight on the bases of the toner weight.

[0210]

In the toner of the present invention, it is preferable for at least some of the toner binder to form a continuous phase and at least some of the charge 10 controlling agent to form discontinuous domains. As compared with the case where the charge controlling agent has complete compatibility with the toner binder without forming the discontinuous domains, the added charge controlling agent is easily exposed to the 15 surface and effective even in a small amount. The dispersion particle diameter of the domain is preferably 0.01 to 4 μm and more preferably 0.05 to 2 μm . If it is bigger than 4 μm , the dispersibility becomes insufficient and the charge level distribution 20 becomes broad and the transparency of the toner is deteriorated. Whereas, if the dispersion particle diameter is smaller than 0.01 μm , it becomes similar to the case where the charge controlling agent has complete compatibility with the binder without forming 25 discontinuous domain, a large amount of the charge controlling agent is required to be added. That at least some of the foregoing charge controlling agent

forms discontinuous domains and the dispersion particle size can be confirmed by observing a thin section specimen of the toner using a transmission electron microscope. In order clearly observe the interface, it
5 is also effective to dye the toner specimen with ruthenium tetraoxide, osmium tetraoxide and the like.

[0211]

Further, for the purpose of reducing the particle diameter of the discontinuous domains formed by
10 polyhydroxyalkanoate according to the present invention, a polymer compatible with the polyhydroxyalkanoate and also with the toner binder may be added as a compatible agent. The compatibility enhancing agent may be a polymer comprising mutually
15 graft- or block-polymerized polymer chains containing at least 50% by mol of monomers having practically similar structure to that of the constituent monomers of polyhydroxyalkanoate according to the present invention and polymer chains containing at least 50% by
20 mol of monomers having practically similar structure to that of the toner binder. The amount of the compatible agent to be used is generally not more than 30% by weight and preferably 1 to 10% by weight, with respect to the polyhydroxyalkanoate according to the present
25 invention.

[0212]

<Other constituent materials>

Other constituent materials constituting the toner of the present invention will be described below.

[0213]

(Binder Resin)

5 First of all, as for the binder resin, any resin may be used without any particular restrictions if it is generally used for production of a toner. Also, the charge controlling agent of the present invention may previously be mixed with the binder resin to be used as
10 a toner binder composition of the present invention having charge controlling capability before production of the toner. For example, as the binder resin, styrene-based polymers, polyester-based polymers, epoxy-based polymers, polyolefin-based polymers, and
15 polyurethane-based polymers, and the like can be exemplified and they are used alone or while being mixed with one another.

[0214]

The styrene-based polymers may be styrene-
20 (meth)acrylic acid ester copolymers and copolymers of these copolymers with other monomers copolymerizable with them; copolymers of styrene with diene type monomers (butadiene, isoprene and the like) and copolymers of these copolymers with other monomers
25 copolymerizable with them; and the like. The polyester-based polymers may be condensation polymerization products of aromatic dicarboxylic acid

and aromatic diol alkylene oxide addition products and the like. The epoxy-based polymers may be reaction products of aromatic diols and epichlorohydrin and their modified products. The polyolefin-based polymers
5 may be polyethylene, polypropylene, and copolymer chains of these polymers with monomers polymerizable with them. The polyurethane-based polymers may be addition polymerization products of aromatic diisocyanates and aromatic diol alkylene oxide addition
10 products and the like.

[0215]

Practical examples of the binder resin to be employed in the present invention are polymers of the following polymerizable monomers or their mixtures or
15 copolymerization products produced from two or more kinds of the following polymerizable monomers. Such polymers are more particularly, for example, styrene-based polymers such as styrene-acrylic acid copolymer, styrene-methacrylic acid copolymer, and the like;
20 polyester-based polymers; epoxy-based polymers; polyolefin-based polymers; and polyurethane-based polymers and they are preferably used.

[0216]

Practical examples of the polymerizable monomers
25 are styrene and its derivatives such as styrene, o-methylstyrene, m-methylstyrene, p-methylstyrene, p-methoxystyrene, p-phenylstyrene, p-chlorostyrene, 3,4-

dichlorostyrene, p-ethylstyrene, 2,4-dimethylstyrene,
p-n-butylstyrene, p-tert-butylstyrene, p-n-
hexylstyrene, p-n-octylstyrene, p-n-nonylstyrene, p-n-
decylstyrene, p-n-dodecylstyrene, and the like;

5 ethylenic unsaturated monoolefins such as ethylene,
propylene, butylene, isobutylene and the like;
unsaturated polyenes such as butadiene and the like;
vinyl halides such as vinyl chloride, vinylidene
chloride, vinyl bromide, vinyl fluoride and the like;

10 vinyl esters such as vinyl acetate, vinyl propionate,
vinyl benzoate and the like; α -methylene aliphatic
monocarboxylic acid esters such as methyl methacrylate,
ethyl methacrylate, propyl methacrylate, n-butyl
methacrylate, isobutyl methacrylate, n-octyl
15 methacrylate, dodecyl methacrylate, 2-ethylhexyl
methacrylate, stearyl methacrylate, phenyl
methacrylate, dimethylaminoethyl methacrylate,
diethylaminoethyl methacrylate, and the like; acrylic
acid esters such as methyl acrylate, ethyl acrylate, n-
20 butyl acrylate, isobutyl acrylate, propyl acrylate, n-
octyl acrylate, dodecyl acrylate, 2-ethylhexyl
acrylate, stearyl acrylate, 2-chloroethyl acrylate,
phenyl acrylate, and the like; vinyl ethers such as
vinyl methyl ether, vinyl ethyl ether, vinyl isobutyl
ether, and the like; vinyl ketones such as vinyl methyl
25 ketone, vinyl hexyl ketone, methyl isopropenyl ketone,
and the like; N-vinyl compounds such as N-vinylpyrrole,

N-vinylcarbazole, N-vinylindole, N-vinylpyrrolidone and
the like; vinyl naphthalenes; acrylic acid or
methacrylic acid derivatives such as acrylonitrile,
methacrylonitrile, acrylamide and the like; the above-
5 described α , β -unsaturated acid esters; bibasic acid
diesters; dicarboxylic acids such as maleic acid,
methyl maleate, butyl maleate, dimethyl maleate,
phthalic acid, succinic acid, terephthalic acid, and
the like; polyols compounds such as ethylene glycol,
10 diethylene glycol, triethylene glycol, 1,2-propylene
glycol, 1,3-propylene glycol, 1,4-butanediol, 1,6-
hexanediol, bisphenol A, hydrogenated bisphenol A,
polyoxyethylene-modified bisphenol A and the like;
isocyanates such as p-phenylene diisocyanate, p-
15 xylylene diisocyanate, 1,4-tetramethylene diisocyanate,
and the like; amines such as ethylamine, butylamine,
ethylenediamine, 1,4-diaminobenzene, 1,4-diaminobutane,
monoethanolamine, and the like; epoxy compounds such as
diglycidyl ether, ethylene glycol diglycidyl ether,
20 bisphenol A glycidyl ether, hydroquinone glycidyl
ether, and the like.

[0217]

(Cross-linking agent)

In the case of producing the binder resin to be
25 employed in the present invention, based on the
necessity, the following cross-linking agent may be
used. Examples of a bifunctional cross-linking agent

are divinylbenzene, bis(4-acryloxyethoxyphenyl)propane, ethylene glycol diacrylate, 1,3-butylene glycol diacrylate, 1,4-butanediol diacrylate, 1,5-pentanediol diacrylate, 1,6-5 hexanediol diacrylate, neopentyl glycol diacrylate, diethylene glycol diacrylate, triethylene glycol diacrylate, tetraethylene glycol diacrylate, respective diacrylates of polyethylene glycol #200, #400, #600, dipropylene glycol diacrylate, polypropylene glycol 10 diacrylate, polyester type diacrylate (MANDA Nippon Kayaku), and those obtained by replacing these exemplified acrylates with methacrylates.

[0218]

Examples of bi- or higher polyfunctional cross-linking agent are pentaerythritol triacrylate, trimethylolethane triacrylate, trimethylolpropane triacrylate, tetramethylolmethane tetraacrylate, oligoester acrylates or methacrylates, 2,2-bis(4-methacryloxy, polyethoxyphenyl)propane, diallyl 20 phthalate, triallyl cyanurate, triallyl azocyanurate, triallyl isocyanurate, diaryl chlorendate, and the like.

[0219]

(Polymerization initiator)

25 In the case of producing the binder resin to be employed in the present invention, the following polymerization initiators may be used based on the

necessity: for example, tert-butyl peroxy-2-ethylhexanoate, cumine perpivalate, tert-butyl peroxylaurate, benzoyl peroxide, lauroyl peroxide, octanoyl peroxide, di-tert-butyl peroxide, tert-5 butylcumyl peroxide, dicumyl peroxide, 2,2'-azobisisobutyronitrile, 2,2'-azobis(2-methylbutyronitrile), 2,2'-azobis(2,4-dimethylvaleronitrile), 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile), 1,1-bis(tert-butylperoxy)-3,3,5-trimethylcyclohexane, 1,1-bis(tert-10 butylperoxy)cyclohexane, 1,4-bis(tert-butylperoxycarbonyl)cyclohexane, 2,2-bis(tert-butylperoxy)octane, n-butyl 4,4-bis(tert-butylperoxy)valirate, 2,2-bis(tert-butylperoxy)butane, 1,3-bis(tert-butylperoxyisopropyl)benzene, 2,5-15 dimethyl-2,5-di(tert-butylperoxy)hexane, 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane, 2,5-dimethyl-2,5-di(benzoylperoxy)hexane, di-tert-butylidiperoxyisophthalate, 2,2-bis(4,4-di-tert-butylperoxycyclohexyl)propane, di-tert-butylperoxy- α -20 methylsuccinate, di-tert-butyl peroxydimethylglutarate, di-tert-butyl peroxyhexahydroterephthalate, di-tert-butyl peroxyazelate, 2,5-dimethyl-2,5-di(tert-butylperoxy)hexane, diethylene glycol bis(tert-butylperoxycarbonate), di-tert-butyl25 peroxytrimethyladipate, tris(tert-butylperoxy)triazine, vinyltris(tert-butylperoxy)silane and the like. Each of these compounds may be used alone or in combination.

The use amount of them is generally in 0.05 parts by weight or more (preferably 0.1 to 15 parts by weight) to 100 parts by weight of monomers.

[0220]

5 (Other biodegradable plastics)

In addition, in the present invention, biodegradable plastics may be preferably used.

Examples of the biodegradable plastics are "Ecostar", "Ecostar plus" (produced by Hagiwara Industries, Inc.), 10 "Biopole" (produced by Monsanto Company), "Ajicoat" (Ajinomoto Co., Ltd.), "Placcel", "Polycaprolactone" (produced by Daicel Chem., Ind., Ltd.), "SHOWLEX", "Bionolle" (produced by Showa Denko K.K.), "Lacty" (produced by Shimadzu Corporation), "Lacea" (produced 15 by Mitsui Chemicals, Inc.) and the like.

[0221]

It is preferable for the combinations of the binder resin and the charge controlling agent of the present invention that the structure of the polymers of 20 the binder resin and the polymer structure of the polymer chain of the charge controlling agent are similar to each other as much as possible. If the structure of the polymers of the binder resin and the polymer structure of the polymer chain of the charge 25 controlling agent are considerably dissimilar to each other, the charge controlling agent tends to be dispersed insufficiently in the binder resin.

[0222]

The weight ratio of the charge controlling agent of the present invention to be internally added to the binder resin is generally 0.1 to 50% by weight,
5 preferably 0.3 to 30% by weight, and more preferably 0.5 to 20% by weight. If the weight ratio of the charge controlling agent to be internally added is lower than 0.1% by weight, the charge level becomes low and if the weight ratio is higher than 50% by weight,
10 the charge stability of the toner is deteriorated.

[0223]

(Coloring agent)

Any coloring agent generally used for production of a toner may be used as the coloring agent composing
15 the toner of the present invention without particular restrictions. For example, carbon black, titanium white, and any other pigment and/or dye may be used.

[0224]

For example, in the case the toner of the present invention is used for a magnetic color toner, examples of the coloring agent to be employed are C.I. Direct Red 1, C.I. Direct Red 4, C.I. Acid Red 1, C.I. Basic Red 1, C.I. Mordant Red 30, C.I. Direct Blue 1, C.I. Direct Blue 2, C.I. Acid Blue 9, C.I. Acid Blue 15,
25 C.I. Basic Blue 3, C.I. Basic Blue 5, C.I. Mordant Blue 7, C.I. Direct Green 6, C.I. Basic Green 4, C.I. Basic Green 6 and the like. Examples of the pigment are

Chrome Yellow, Cadmium Yellow, Mineral Fast Yellow,
Naple's Yellow, Naphthol Yellow S, Hansa Yellow G,
Permanent Yellow NCG, Tartrazine Yellow Lake, Chrome
Orange, Molybenum Orange, Permanent Orange GTR,
5 Pyrazolone Orange, Benzidine Orange G, Cadmium Red,
Permanent Red 4R, Watching Red calcium salt, Eosine
Lake, Brilliant Carmine 3B, Manganese Violet, Fast
Violet B, Methyl Violet Lake, Prussian Blue, Cobalt
Blue, Alkali Blue Lake, Victoria Blue Lake,
10 Phthalocyanine Blue, Fast Sky Blue, Indanthrene Blue
BC, Chrome Green, chromium oxide, Pigment Green B,
Malachite Green Lake, Final Yellow Green G and the
like.

[0225]

15 In the case the toner of the present invention is
used for a two-component type full color toner, the
following coloring agents can be used. For example,
coloring pigments for magenta toners are C.I. Pigment
Red 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15,
20 16, 17, 18, 19, 21, 22, 23, 30, 31, 32, 37, 38, 39, 40,
41, 48, 49, 50, 51, 52, 53, 54, 55, 57, 58, 60, 63, 64,
68, 81, 83, 87, 88, 89, 90, 112, 114, 122, 123, 163,
202, 206, 207, 209, C.I. Pigment Violet 19, C.I. Vat
Red 1, 2, 10, 13, 15, 23, 29, 35 and the like.

25 [0226]

In the present invention, the above-exemplified
pigments may be used alone, but it is more preferable

that they are used in combination with dyes for improving the clearness from the aspect of the full color image quality. In such a case, the examples of usable magenta dyes are oil-soluble dyes such as C.I.

5 Solvent Red 1, 3, 8, 23, 24, 25, 27, 30, 49, 81, 82,
83, 84, 100, 109, 121, C.I. Disperse Red 9, C.I.
Solvent Violet 8, 13, 14, 21, 27, C.I. Solvent Violet
8, 13, 14, 21, 27, and C.I. Disperse Violet 1 and the
like; and basic dyes such as C.I. Basic Red 1, 2, 9,
10 12, 13, 14, 15, 17, 18, 22, 23, 24, 27, 29, 32, 34, 35,
36, 37, 38, 39, 40, C.I. Basic Violet 1, 3, 7, 10, 14,
15, 21, 25, 26, 27, 28 and the like.

[0227]

As other coloring pigments, examples of cyan
15 coloring pigments are C.I. Pigment Blue 2, 3, 15, 16,
17, C.I. Vat Blue 6, C.I. Acid Blue 45, copper-
phthalocyanine pigments having a phthalocyanine
skeleton containing substituents of phthalimidomethyl
groups in number of 1 to 5, and the like.

20 [0228]

Examples of yellow coloring pigments are C.I.
Pigment Yellow 1, 2, 3, 4, 5, 6, 7, 10, 11, 12, 13, 14,
15, 16, 17, 23, 65, 73, 83, C.I. Vat Yellow 1, 3, 20
and the like.

25 [0229]

The above-described dyes and pigments may be used
solely or may be used while being optionally mixed with

one another to obtain desired hue of the toner. When considering the environmental conservation and the safety to the human body, various food colors can be suitably used. The content of the coloring agents in
5 the toner may be widely altered depending on the desired coloration effects. Generally, in order to obtain the best toner properties, that is, in consideration of the printing coloration capability, the toner shape stability, and the toner scattering,
10 these coloring agents are used at a ratio in the range of from 0.1 to 60 parts by weight, preferably 0.5 to 20 parts by weight with respect to 100 parts by weight of the binder resin.

[0230]

15 <Other components of toner>

In the toner of the present invention may contain the following compounds other than the foregoing binder resin and the coloring agent components, to an extent (within a ratio less than the content of the binder resin) in which no undesired effect is caused in the present invention. Examples of such compounds include silicone resin; polyester; polyurethane; polyamide; epoxy resin; poly(vinyl butyral); rosin; modified rosin; terpene resin; phenolic resin; aliphatic or
20 alicyclic hydrocarbon resin such as lower molecular weight polyethylene and lower molecular weight polypropylene; aromatic type petroleum resin; and
25

chlorinated paraffin and paraffin waxes. Among them, preferable waxes to be used are practically lower molecular weight polypropylene and its byproducts, lower molecular weight polyester, and ester type wax
5 and aliphatic derivatives. Among these waxes, waxes fractionated based on the molecular weight of the waxes by various methods are also preferably used in the present invention. Further, after fractionation, the waxes may be modified to control the acid values,
10 block-copolymerized, or graft-modified.

[0231]

Specially, in the toner of the present invention, in the case such wax components as described above are added and these wax components are found practically
15 dispersed in the binder resin in spherical and/or spindly island state when the section of the toner was observed by a transmission electron microscope, the toner has excellent properties.

[0232]

20 <Method of producing toners>

Any conventionally known method may be employed for a practical method for producing a toner of the present invention having the constitution as described above. The toner of the present invention can be
25 produced, for example, by a so-called pulverization method for obtaining a toner through the following steps. Specifically, the above-described

polyhydroxyalkanoate, resin materials such as binder resin, and a wax to be added as necessary, , are sufficiently mixed by a mixer such as a Henshel mixer, a ball mill and the like and then melted and kneaded
5 using a thermally kneading apparatus such as heating rolls, a kneader, an extruder and the like to make the resin material compatible with one another, and as coloring agents, pigments, dyes, or magnetic materials and also additives such as metal compounds to be added
10 as necessary are dispersed or dissolved in the resulting mixture, and after solidification of the mixture by cooling, the obtained solidified product is pulverized by a pulverizing apparatus such as a jet mill, a ball mill and the like and then classified to
15 obtain an toner of the present invention with a desired particle size. In the above-described classification step, from an aspect of productivity, a multi-step classification apparatus is preferably used.

[0233]

20 In addition, the toner of the present invention with a desired particle size can be obtained by mixing and stirring the binder resin and the above-described polyhydroxyalkanoate in a solvent (e.g., aromatic hydrocarbons such as toluene, xylene and the like; halogen compounds such as chloroform, ethylene
25 dichloride, and the like; ketones such as acetone, methyl ethyl ketone, and the like; amides such as

dimethylformamide and the like), and then adding the resulting mixture to water to re-precipitate the solid, then filtering and drying the solid, and further pulverizing it by a pulverizing apparatus such as a jet mill, a ball mill, and the like, and finally classifying the pulverized matter. In the above-described classification step, from an aspect of productivity, a multi-step classification apparatus is preferably used.

10 [0234]

In addition, the toner of the present invention can be produced by a so-called polymerization method as follows. That is, in this case, the above-described polyhydroxyalkanoate, a polymerizable monomer, and as coloring agents, pigments, dyes, or magnetic materials and also based on the necessity, additives such as a cross-linking agent, a polymerization initiator, waxes, other additives, and others are mixed and dispersed and in the presence of a surfactant or the like, the mixture is subjected to suspension polymerization to obtain a polymerized and colored resin particles, and after the obtained particles are separated by solid-liquid separation, the particles are dried and classified if necessary to obtain a toner of the present invention with a desired particle size.

[0235]

Furthermore, colored fine particles containing no

charge controlling agent is produced by the above-described manner and then either solely or together with an externally added agent such as colloidal silica, the above polyhydroxyalkanoate may be attached 5 and fixed to the surface of the particle by a mechanochemical method or the like.

[0236]

(Externally added silica agent)

In the present invention, a silica fine powder is 10 preferably added externally to the toner produced in a manner as described above for improving the charge stability, development characteristic, fluidity and durability. The silica fine powder to be employed in this case can provide desirable effects if it has a 15 specific surface area of 20 m²/g or higher (especially 30 to 400 m²/g) measured based on the nitrogen adsorption by the BET method. The content of the silica fine powder to be added is preferably 0.01 to 8 parts by weight, more preferably 0.1 to 5 parts by 20 weight, with respect to 100 parts by weight of the toner particles. In this case, based on the necessity, the silica fine powder to be used in the case is preferably treated, for the purpose of controlling the hydrophobicity and charge properties, with silicone 25 varnish, variously modified silicone varnish, silicone oil, variously modified silicone oil, a silane coupling agent, a silane coupling agent having a functional

group, and other organosilicon compounds. These treatment agents may be used by mixing.

[0237]

(Inorganic powder)

5 Further, in order to improve the development capability and the durability, the following inorganic powder is preferably added. Examples of the powder are oxides of metals such as magnesium, zinc, aluminum, cerium, cobalt, iron, zirconium, chromium, manganese, 10 strontium, tin, antimony and the like; compounded metal oxides such as calcium titanate, magnesium titanate, and strontium titanate; metal salts such as calcium carbonate, magnesium carbonate, and aluminum carbonates; clay minerals such as kaolin; phosphate 15 compounds such as apatite; silicon compounds such as silicon carbide, and silicon nitride; and carbon powder such as carbon black and graphite. Among them, fine powders of zinc oxide, aluminum oxide, cobalt oxide, manganese dioxide, strontium titanate, and magnesium 20 titanate are preferably used.

[0238]

(Lubricant)

Further, the following lubricant powder may be added to the toner. For example, fluoro resin such as 25 Teflon, poly(vinylidene fluoride) and the like; fluoride compounds such as carbon fluoride; aliphatic acid metal salts such as zinc stearate; aliphatic acid

derivatives such as aliphatic acid, aliphatic acid esters and the like; and molybdenum sulfide.

[0239]

<Carrier>

5 The toner of the present invention having the above-described constitution is usable for a variety of conventionally known toners; solely as a non-magnetic one-component developer, as a non-magnetic toner together with a magnetic carrier for composing a
10 magnetic two-component developer, as a magnetic toner to be used solely for a magnetic mono-component toner. In this case, as the carrier to be used for the two-component development, any conventionally known carrier may be used. More particularly, particles of surface-
15 oxidized or non-oxidized metals such as iron, nickel, cobalt, manganese, chromium and rare earth metals, their alloys and oxides and having an average particle size of 20 to 300 μm may be used as the carrier particles. Further, the carrier to be used in the
20 present invention are preferably the above-described carrier particle whose surface bears or is coated with a substance such as styrene-based resin, acrylic resin, silicone resin, fluoro resin, polyester resin and the like.

25 [0240]

<Magnetic toner>

The toner of the present invention may be a

magnetic toner by adding a magnetic material to the toner particles. In this case, the magnetic material may take a role also as a coloring agent. The magnetic material to be used in this case may be iron oxides
5 such as magnetite, hematite, and ferrite; metals such as iron, cobalt, and nickel; alloys of these metals with metals such as aluminum, cobalt, copper, lead, magnesium, tin, zinc, antimony, beryllium, bismuth, cadmium, calcium, manganese, selenium, titanium,
10 tungsten, and vanadium; and their mixtures. The magnetic material to be used in the present invention has an average particle size preferably 2 μm or smaller, more preferably 0.1 to 0.5 μm . The amount to be added to the toner is preferably 20 to 200 parts by
15 weight to 100 parts by weight of the binder resin and especially preferably 40 to 150 parts by weight to 100 parts by weight of the binder resin.

[0241]

In addition, in order to give high image quality,
20 it is required to precisely develop very small latent image dots and for this purpose, for example, it is preferable that the weight average particle size of the toner of the present invention is controlled so that it is in the range of from 4 to 9 μm . That is, if the
25 toner particle has a weight average particle size smaller than 4 μm , the transfer efficiency is decreased and a large amount of the transfer residual toner tends

to remain on a photoconductor to result in an undesirable cause of uneven and irregular image formation due to fogging and transfer failures.

Whereas, if the toner particle has a weight average
5 particle size larger than 9 μm , scattering around letters and line images tends to occur.

[0242]

In the present invention, the average particle size and the particle size distribution of the toner
10 are measured by using Coulter Counter TA-II model or Coulter Multisizer (manufactured by Coulter Co.) or the like to which an interface (manufactured by Nikka Machine Co.) for outputting the distribution by number, the distribution by volume and a PC9801 personal
15 computer (manufactured by NEC) are connected. As an electrolytic solution to be used at that time, an aqueous 1% NaCl solution is prepared using first-grade sodium chloride. As the electrolytic solution, for example, a commercialized ISOTON R-II (produced by
20 Coulter Scientific Japan Co.) may also be usable. A practical measurement method involves steps of adding 0.1 to 5 mL of a surfactant (preferably an alkylbenzenesulfonic acid salt is used) as a dispersant to 100 to 150 mL of the above-described aqueous
25 solution, further adding 2 to 20 mg of a sample to the resulting solution to obtain a specimen to be measured. At the time of measurement, the electrolytic solution

in which the specimen to be measured is suspended is
treated for dispersion for 1 to 3 minutes by an
ultrasonic dispersing apparatus and then the volume and
the number of the toner particles of 2 μm or larger are
5 measured by the foregoing Coulter Counter TA-II model
using 100 μm aperture and the distribution by volume
and the distribution by number are calculated. Then,
the weight average particle size (D4) on the basis of
the volume calculated from the distribution by volume
10 according to the present invention and the length
average particle size (D1) on the basis of the number
calculated from the distribution by number are
calculated.

[0243]

15 <Charge level>

In addition, the charge level of the toner of the
present invention is preferably in the range of from -
10 to -80 $\mu\text{C/g}$, more preferably from -15 to -70 $\mu\text{C/g}$
per unit weight (two-component method) in improving the
20 transfer efficiency in a transfer method using a
transfer member with a voltage applied thereto.

[0244]

The method of measuring an charge level (a two-
component tribo) by the two-component method employed
25 in the present invention will be described as follows.
A charge level measuring apparatus illustrated in
Figure 11 is used for the measurement. At first, under

a specified environment, EFV 200/300 (produced by Powder Tec Co.) is used as a carrier and a bottle made of a polyethylene with a capacity of 50 to 100 mL is charged with a mixture of 9.5 g of the carrier and 0.5 5 g of a toner to be measured, set in a shaking apparatus so controlled as to keep the amplitude constant, and shaken for a prescribed period in the shaking conditions of an amplitude of 100 mm and a shaking speed of 100 rpm. Then, 1.0 to 1.2 g of the above 10 mixture is placed in a measurement container 42 made of metal having a 500-mesh screen 43, and the measurement container 42 is covered with a metal lid 44 in the bottom of the charge level measuring apparatus shown in Figure 11. The total weight of the measurement 15 container 42 at that time is measured and determined as W_1 (g). Next, the gas in the container is aspirated through a suction port 47 by an unillustrated aspirator (at least the portion contacting the measurement container 42 is made of an insulator) and an air 20 ventilation adjustment valve 46 is controlled to control the pressure of the vacuum meter 45 to be 2,450 Pa (250 mmAq). Under such a state, aspiration is carried out for 1 minute to suck and remove the toner. The potential of a potentiometer 49 at that time is 25 denoted as V (volt). The reference numeral 48 denotes a capacitor and the capacity is denoted as C (μF). The weight of the entire measurement container after the

aspiration is weighed and denoted as W2 (g). The friction charge level ($\mu\text{C/g}$) of the toner can be calculated according to the following equation from these measurement values.

5 Friction charge level ($\mu\text{C/g}$) = $C \times V / (W_1 - W_2)$

<Molecular weight distribution of binder resin>

The binder resin for use in the constituent material of the toner of the present invention preferably has a peak within the range of from 3,000 to 10 15,000 in a low molecular weight region of the molecular weight distribution measured by GPC, especially, in the case of production by the pulverization method. That is, if the GPC peak exceeds 15,000 in the low molecular weight region, it sometimes becomes difficult to obtain a toner with a sufficiently improved transfer efficiency. Whereas if binder resin having a GPC peak of less than 3,000 is used, melting 15 takes place easily at the time of surface treatment and therefore it is undesirable.

20 [0245]

In the present invention, the molecular weight of the binder resin is measured by GPC (gel permeation chromatography). A practical GPC measurement method is carried out as follows: a toner previously extracted 25 with THF (tetrahydrofuran) solvent for 20 hours using a Soxhlet extractor is used as a sample for measurement. Using columns A-801, 802, 803, 804, 805, 806, and 807

manufactured by Showa Denko K.K. and the calibration curve of standardized polystyrene resins, the molecular weight distribution is measured. Further, in the present invention, it is preferable that the binder resin with the ratio (M_w/M_n) of the weight average molecular weight (M_w) to the number average molecular weight (M_n) measured as described above being in the range of from 2 to 100 is used.

[0246]

10 <Glass transition temperature of toner>

Further, the toner of the present invention is preferably adjusted by using a proper material so as to have a glass transition temperature T_g in the range of from 40 to 75°C, more preferably 52 to 70°C, from a viewpoint of fixation and storage stability. In this case, the measurement of the glass transition temperature T_g may be carried out using a high precision and internally heating input compensation type differential scanning calorimeter, for example, DSC-7 manufactured by Perkin Elmer Co., may be employed. The measurement method is carried out according to ASTM D3418-82. In the present invention, when the glass transition temperature T_g is measured, it is preferable that a measurement sample is once heated to cancel the entire hysteresis and then cooled rapidly and again heated at a heating rate of 10°C/min to employ the DSC curve measured during the heating

from 0 to 200°C.

[0247]

<Image formation method>

The toner of the present invention having the
5 configuration described above is particularly
preferably applied to an image formation method, the
method comprising at least an charging step of applying
a voltage to a charging member from the outside to
charge an electrostatic latent image-holding member, a
10 step of forming an electrostatic latent image on the
charged electrostatic latent image-holding member, a
development step of developing the electrostatic latent
image with the toner to form a toner image on the
electrostatic latent image-holding member, a transfer
15 step of transferring the toner image on the
electrostatic latent image-holding member to a
recording material, and a heat-fixation step of heat-
fixing the toner image on the recording material.
Alternatively, an image formation method can be used
20 where the transfer step consists of a first transfer
step of transferring the toner image on the
electrostatic latent image-holding member to an
intermediate transfer member and a second transfer step
of transferring the toner image on the intermediate
25 transfer member to the recording material.

[0248]

[Examples]

Next, the present invention is described further specifically with reference to Examples and Comparative Examples. It should be noted that these Examples are illustrative of the best mode of the embodiment of the 5 present invention and do not limit the present invention. Further, all parts in the following formulations are by mass.

[0249]

[PHA]

10 First, as a method for preparing a charge controlling agent according to the present invention, a method for preparing polyhydroxyalkanoate of the present invention comprising a microbiological production step and a chemical processing step is shown 15 below (Examples A-1 to A-4).

[0250]

(Example A-1)

A culture medium containing 5-(4-vinylphenyl)valeric acid as an ω -(4-vinylphenyl)alkanoic acid represented by general formula (17) and 5-phenylvaleric acid as an ω -substituted alkanoic acid represented by general formula (18), and polypeptone as a peptide source was prepared as follows: 5.0 g of polypeptone (Wako Pure 25 Chemicals Industries, Ltd.) and 0.8912 g of 5-phenylvaleric acid were dissolved in 1000 mL of the above M9 culture medium, put in a 2000 mL shaking

flask, and sterilized by an autoclave. After the above heat sterilization treatment, the mixture was cooled to room temperature, and 0.2043 g of 5-(4-vinylphenyl)valeric acid was added. Then, the 5 resultant mixture was sufficiently stirred to prepare a culture medium.

[0251]

Pseudomonas cichorii YN2 strain was inoculated in an M9 culture medium containing 0.5% of polypeptone and 10 shake-cultured at 30°C for 8 hours to prepare a preculture. 5 mL of this preculture solution was added to the above culture medium containing 5-(4-vinylphenyl)valeric acid and 5-phenylvaleric acid as substrates to culture the cells at 30°C for 39 hours. 15 After being cultured, the cells were collected by centrifugation, washed with methanol, and then lyophilized.

[0252]

After dried cells were weighed, chloroform was 20 added. The mixture was stirred at 25°C for 72 hours, thereby extracting the polymer accumulated in the cell. The chloroform solution with the extracted polymer dissolved therein was filtered. The chloroform filtrate was concentrated by an evaporator, followed by 25 redissolving the polymer in acetone and filtering off insoluble components. Then, the filtrate was concentrated by an evaporator, and precipitated solid

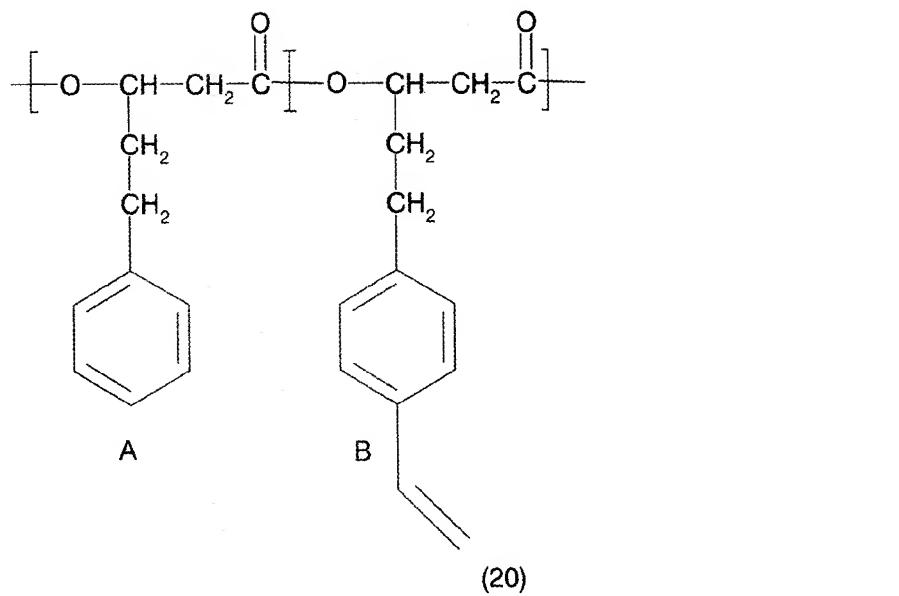
components were collected with cold methanol. The components were dried under a reduced pressure to collect the desired polymer. The dry weight of the polymer collected in the above collection step was
5 measured.

[0253]

The structure of the collected polymer was determined by $^1\text{H-NMR}$ (FT-NMR: Bruker DPX400; ^1H resonance frequency: 400 MHz; measurement nuclear
10 species: ^1H ; solvent used: CDCl_3 ; reference: capillary-encapsulated TMS/ CDCl_3 ; measurement temperature: room temperature) to find that the polymer was a polyhydroxyalkanoate copolymer containing units represented by the following formula (20)

15 [0254]

[Chemical Formula 103]



[0255]

in a content ratio (mol%) of A:B = 83:17. The ¹H-NMR spectrum of the resultant polymer is shown in Figure 1.

5 [0256]

In addition, the average molecular weight of the polymer was measured by gel permeation chromatography (GPC) (Tosoh HLC-8220 GPC; column: Tosoh TSK-GEL SuperHM-H; solvent; chloroform; polystyrene equivalent).

10 [0257]

Dry weight of the cells obtained in the above step, dry weight of the collected polymer, weight ratio of the collected polymer to dried cells, and the number 15 average molecular weight, the weight average molecular weight, and the molecular weight distribution of the

resultant polymer are shown together in Table 1.

[0258]

[Table 1]

Table 1: Productivity of polymer

CDW (mg/L)	PDW (mg/L)	P/C %	Mn ($\times 10^4$)	Mw ($\times 10^4$)	Mw/Mn
1205	600	49.8	5.9	12.1	2.1

5 [0259]

CDW: dry weight of cells; PDW: dry weight of polymer;

P/C: dry weight of cells/dry weight of polymer;

Mn: number average molecular weight; Mw: weight average molecular weight;

10 Mw/Mn: molecular weight distribution

[0260]

(Example A-2)

Under a nitrogen atmosphere, 0.3061 g of polyester containing a 3-hydroxy- ω -(4-vinylphenyl)valeric acid unit, 0.1923 g of 18-crown-6-ether, and 10.0 mL of dichloromethane were added to a 100 mL flask followed by stirring. The flask was dipped in an ice bath to cool the reaction system to 0°C. After 30 minutes, 0.1517 g of potassium permanganate was added. The 20 reaction vessel was wrapped with aluminum foil followed by stirring for 21 hours. After the reaction was completed, water having sodium bisulfite dissolved therein was added, and the reaction solution was reprecipitated in methanol to collect the polymer. The

polymer obtained here was dialyzed by using chloroform for purification.

[0261]

The structure of the resultant polymer was determined by $^1\text{H-NMR}$ (FT-NMR: Bruker DPX400; resonance frequency: 400 MHz; measurement nuclear species: ^1H ; solvent used: deuterated chloroform; measurement temperature: room temperature) and analyzed by Fourier transform infrared absorption (FT-IR) spectrum (Nicolet 10 AV ATAR360 FT-IR). As the result, an additional absorption derived from carboxylic acid was found at 1693 cm^{-1} , and hence it was found that the resultant PHA had a 3-hydroxy- ω -(4-carboxyphenyl)valeric acid unit. The $^1\text{H-NMR}$ spectrum of the resultant polymer is shown in Figure 2.

[0262]

Further, in order to calculate the units of the resultant PHA, the calculation was performed by methyl-esterifying a carboxyl group on the end of the side chain of PHA by using trimethylsilyldiazomethane.

[0263]

30 mg of the desired product of PHA was added to a 100 mL round bottomed flask, and then 2.1 mL of chloroform and 0.7 mL of methanol were added and dissolved. To the mixture, 0.5 mL of 2 mol/L trimethylsilyldiazomethane-hexane solution (Aldrich) was added followed by stirring at room temperature for

30 minutes. After the reaction was completed, the solvent was distilled off by an evaporator to collect the polymer. After washing with 50 mL of methanol, the polymer was collected. 32 mg of PHA was obtained by
5 drying under a reduced pressure.

[0264]

From the result of NMR analysis in the similar manner of the above method, it was confirmed that the resultant PHA contains 17 mol% of a 3-hydroxy- ω -(4-
10 carboxyphenyl)valeric acid unit.

[0265]

(Example A-3)

Three 2000 mL shaking flasks were prepared. 0.5 wt% of polypeptone (Wako Pure Chemicals Industries,
15 Ltd.), 6.0 mmol/L of 5-(phenylsulfanyl)valeric acid, and 1 mmol/L of 5-(4-vinylphenyl)valeric acid were dissolved in 1000 mL of the above M9 culture medium, charged in each of the 2000 mL shaking flask, and sterilized by an autoclave followed by cooling to the
20 room temperature. To each of the prepared culture medium, 10 mL of a culture solution of *Pseudomonas cichorii* YN2 precultured in an M9 medium containing 0.5% of polypeptone with shaking for 8 hours was added, and the mixture was cultured at 30°C for 38 hours.
25 After being cultured, the culture was pooled, and cells were collected by centrifugation, washed with methanol, and then dried. After the weight of the dried cells

was weighed, chloroform was added. The mixture was stirred at 35°C for 25 hours, thereby extracting the polymer. The chloroform from which the polymer was extracted was filtered by a 0.45 µm membrane filter,
5 concentrated by an evaporator, and then reprecipitated in cold methanol to collect the polymer. Thereafter, the polymer was dried under a reduced pressure to obtain the desired polymer.

[0266]

10 As the result of weighing the resultant polymer, 1111 mg (dry weight) of PHA was obtained in this example.

[0267]

15 The average molecular weight of the resultant PHA was evaluated by gel permeation chromatography (GPC; Tosoh HLC-8220; column: Tosoh TSK-GEL SuperHM-H; solvent; chloroform; polystyrene equivalent). The result showed that the number average molecular weight Mn was 105000.

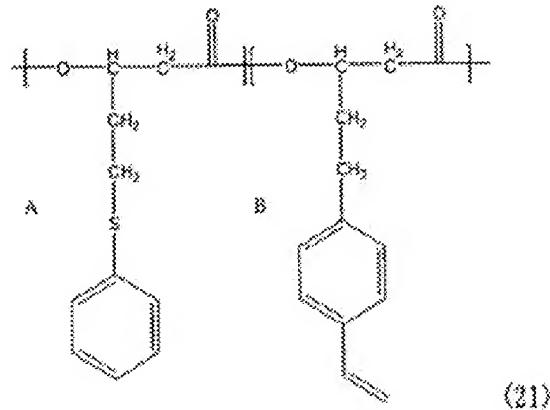
20 [0268]

Further, in order to determine the structure of the resultant PHA, NMR analysis was performed under the similar condition as in Example A-1. The ¹H-NMR spectrum of the resultant polymer is shown in Figure 3.
25 As the result, the PHA was found to be a polyhydroxyalkanoate copolymer containing a 3-hydroxy-5-(phenylsulfanyl)valeric acid unit and a 3-hydroxy- ω -

(4-vinylphenyl)valeric acid unit as monomer units as represented by the following chemical formula (21).

[0269]

[Chemical Formula 104]



(21)

5

[0270]

Moreover, the proportion of the units was confirmed by $^1\text{H-NMR}$ spectrum to be 70 mol% of 3-hydroxy-5-(phenylsulfanyl)valeric acid, 20 mol% of 3-hydroxy- ω -(4-vinylphenyl)valeric acid, and 10 mol% of the others (straight-chained 3-hydroxyalkanoic acid having 4 to 12 carbon atoms).

[0271]

(Example A-4)

15 302 mg of polyhydroxyalkanoate obtained in Example A-3 was added to a 200 mL round bottomed flask, and then 20 mL of dichloromethane was added and dissolved. The mixture was placed in an ice bath, and 3 mL of acetic acid and 1103 mg of 18-crown-6-ether were added 20 followed by stirring. Next, 877 mg of potassium

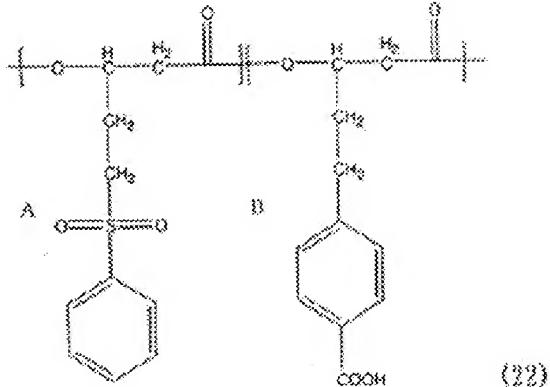
permanganate was gradually added to the flask in an ice bath followed by stirring at room temperature for 21 hours. After the reaction was completed, 50 mL of water and 3050 mg of sodium bisulfite were added.

5 Then, the solution was made to be pH 1 by adding 1.0 mol/L (1.0 N) hydrochloric acid. After dichloromethane in the mixed solution was distilled off by an evaporator, the polymer in the solution was collected. The polymer was washed with 150 mL of pure water, 150 mL of methanol, 150 mL of pure water 2 times, and 50 mL of methanol in this order followed by collecting the polymer. The polymer was dried under a reduced pressure to obtain 342 mg of the desired PHA.

Further, in order to determine the construction of 15 the resultant PHA, analysis was performed by $^1\text{H-NMR}$ (FT-NMR: Bruker DPX400; resonance frequency: 400 MHz; measurement nuclear species: ^1H ; solvent used: dDMSO; measurement temperature: room temperature). The $^1\text{H-NMR}$ spectrum of the resultant polymer is shown in Figure 4. 20 As the result, the polymer was found to be a polyhydroxyalkanoate copolymer containing a 3-hydroxy-5-(phenylsulfonyl)valeric acid unit and a 3-hydroxy- ω -(4-carboxyphenyl)valeric acid unit as monomer units as represented by the following chemical formula (22).

25 [0272]

[Chemical Formula 105]



(22)

[0273]

Further, in order to calculate the units of the resultant PHA, the calculation was performed by methyl-
5 esterifying a carboxyl group on the end of the side chain of PHA by using trimethylsilyldiazomethane.

[0274]

30 mg of the desired product of PHA was added to a 100 mL round bottomed flask, and then 2.1 mL of
10 chloroform and 0.7 mL of methanol were added and dissolved. To the mixture, 0.5 mL of 2 mol/L trimethylsilyldiazomethane-hexane solution (Aldrich) was added followed by stirring at room temperature for 30 minutes. After the reaction was completed, the
15 solvent was distilled off by an evaporator to collect the polymer. After washing with 50 mL of methanol, the polymer was collected. 31 mg of PHA was obtained by drying the polymer under a reduced pressure.

[0275]

20 NMR analysis was performed in the same manner as

described above. As a result, $^1\text{H-NMR}$ spectrum confirmed that the proportion of the units is 74 mol% of 3-hydroxy-5-(phenylsulfonyl)valeric acid, 17 mol% of a 3-hydroxy- ω -(4-carboxyphenyl)valeric acid unit, and 5 9 mol% of the others (straight-chained 3-hydroxyalkanoic acid having 4 to 12 carbon atoms).

[0276]

The compound obtained as in Example A-2 was referred to as exemplary compound (1) and the compound 10 obtained as in Example A-3 as exemplary compound (S1), and they were used in Example B-1 or later.

[0277]

Next, charge controlling agents produced as in Examples A-2 and A-4 in the manner selected from the 15 methods of the present invention were used as to produce various toners and evaluated (Examples B-1 to B-16 and C-1 to C-16).

[0278]

(Example B-1)

20 First, an aqueous Na_3PO_4 solution was added in a 2 liter four-necked flask equipped with a high-speed stirring apparatus TK-Homomixer, and heated to 60°C with stirring at 10,000 rpm. An aqueous CaCl_2 solution was slowly added therein to prepare a water based 25 dispersing medium containing a very small low-water solubility dispersant $\text{Ca}_3(\text{PO}_4)_2$.

[0279]

On the other hand, the following composition was dispersed for 3 hours using a ball mill, followed by adding therein 10 parts by mass of a release agent (ester wax) and 10 parts by mass of 2,2'-azobis(2,4-5 dimethylvaleronitrile) as a polymerization initiator to prepare a polymerizable monomer composition.

[0280]

- Styrene monomer 82 parts by mass
- Ethylhexyl acrylate monomer 18 parts by mass
- 10 · Divinylbenzene monomer 0.1 parts by mass
- Cyan coloring agent (C.I. Pigment Blue 15)
 - 6 parts by mass
- Oxidized polyethylene resin (molecular weight 3200, acid number 8) 5 parts by mass
- 15 · Exemplary compound (1) 2 parts by mass

[0281]

Then, the polymerizable monomer composition obtained as described above was charged in the water based dispersant prepared previously to form particles 20 with the number of rotations being kept at 10,000 rpm. Thereafter, the composition was made to undergo a reaction at 65°C for 3 hours while being stirred with a paddle stirring blade, and thereafter polymerized at 80°C for 6 hours to complete the polymerization 25 reaction. After the reaction was completed, the suspension was cooled, and an acid was added therein to dissolve the low-water solubility dispersant $\text{Ca}_3(\text{PO}_4)_2$,

followed by filtration, rinsing and drying to obtain blue polymerized particles (1). The particle size of the obtained blue polymerized particles (1) measured using Coulter Counter Multisizer (from Coulter Co.) was 5 6.8 μm (weight average particle size), and the ratio of fines was 4.9% by number.

[0282]

As a fluidity improver, 1.3 parts by mass of hydrophobic silica fine powder (BET: 270 m^2/g) treated 10 with hexamethyl disilazane were externally added to 100 parts by mass of blue polymerized particles(1) prepared as described above through dry-mixing by a Henshel mixer, whereby a blue toner (1) of this Example was obtained. In addition, 7 parts by mass of blue toner 15 (1) were mixed with 93 parts by mass resin-coated magnetic ferrite carrier (average particle size: 45 μm) to prepare a two-component type blue developer (1) for magnetic brush development.

(Example C-1)

20 Blue toner (S1) of Example C-1 was obtained in the same manner as in Example B-1 except that 2 parts by mass of an exemplary compound (S1) are used in place of an exemplary compound (1). In addition, two-component type blue developer (S1) was obtained in the same 25 manner as in Example B-1 using the blue toner.

[0283]

(Comparative Example B-1)

A blue toner (2) of Comparative Example B-1 was obtained in the same manner as in Example B-1 except that no exemplary compound was used. The properties of this toner were measured in the same manner as in 5 Example B-1, and the results thereof are shown in Table 2. In addition, a two-component type blue developer (2) of Comparative Example B-1 was obtained in the same manner as in Example B-1 using this toner.

[0284]

10 <Evaluation>

For the two-component type blue developers (1), (S1) obtained in the above Examples B-1, C-1 and the two-component type blue developer (2) obtained in Comparative Example B-1, the charge levels of the 15 toners after stirring for 10 and 300 seconds were measured under conditions of normal temperature and normal humidity (25°C, 60% RH) and high temperature and high humidity (30°C, 80% RH) using the previously described method for measuring charge levels. Then, 20 numbers from measurement values of two-component blow-off charge levels were rounded off to the first decimal place to make evaluations according to the following criteria. The results are shown together in Table 2.

[0285]

25 [Electrifiability]

AA: Excellent (-20 µC/g or lower)

A: Good (-19.9 to -10.0 µC/g)

B: Usable (-9.9 to -5.0 $\mu\text{C/g}$)

C: Unusable (-4.9 $\mu\text{C/g}$ or higher)

[0286]

(Examples B-2, C-2)

5 Yellow toners (1) and (S1) of Examples B-2 and C-2
were obtained in the same manner as in Example B-1
except that 2.0 parts by mass of exemplary compounds
(1) and (S1) were used respectively, and a yellow
coloring agent (Hansa yellow G) was used in place of
10 the cyan coloring agent. The properties of these
toners were measured in the same manner as in Example
B-1, and the results thereof are shown in Table 2. In
addition, two-component type yellow developers (1),
(S1) were obtained in the same manner as in Example B-1
15 using these toners.

[0287]

(Comparative Example B-2)

A yellow toner (2) of Comparative Example B-2 was
obtained in the same manner as in Example B-1 except
20 that an exemplary compound was not used, and that the
yellow coloring agent (Hansa yellow G) was used in
place of the cyan coloring agent. The properties of
this toner were measured in the same manner as in
Example B-1, and the results thereof are shown in Table
25 2. In addition, a two-component type yellow developer
(2) of Comparative Example B-2 was obtained in the same
manner as in Example B-1 using this toner.

[0288]

<Evaluation>

For the two-component type yellow developers (1),
(S1) obtained in the Examples B-2, C-2 and the two-
5 component type yellow developer (2) obtained in the
Comparative Example B-2, the charge levels of toners
after stirring for 10 and 300 seconds were measured
under conditions of normal temperature and normal
humidity (25°C, 60% RH) and high temperature and high
10 humidity (30°C, 80% RH) using the previously described
method of measuring charge levels. Then, numbers from
measurement values of two-component blow-off charge
levels were rounded off to the first decimal place to
make evaluations according to the following criteria.
15 The results are shown together in Table 2.

[0289]

<Electrifiability>

AA: Excellent (-20 µC/g or lower)
A: Good (-19.9 to -10.0 µC/g)
20 B: Usable (-9.9 to -5.0 µC/g)
C: Unusable (-4.9 µC/g or higher)

[0290]

(Examples B-3, C-3)

Black toners (1) and (S1) of Examples B-3 and C-3
25 were obtained in the same manner as in Example B-1
except that 2.0 parts by mass of exemplary compounds
(1) and (S1) were used respectively, and a carbon black

(DBP oil absorption 110 mL/100 g) was used in place of the cyan coloring agent. The properties of these toners were measured in the same manner as in Example B-1, and the results thereof are shown in Table 2. In 5 addition, two-component type black developers (1) and (S1) were obtained in the same manner as in Example B-1 using these toners.

[0291]

(Comparative Example B-3)

10 A black toner (2) of Comparative Example B-3 was obtained in the same manner as in Example B-1 except that an exemplary compound was not used, and that the carbon black (DBP oil absorption 110 mL/100 g) was used in place of the cyan coloring agent. The properties of 15 this toner were measured in the same manner as in Example B-1, and the results thereof are shown in Table 2. In addition, a two-component type black developer (2) of Comparative Example B-3 was obtained in the same manner as in Example B-1 using this toner.

20 [0292]

<Evaluation>

For the two-component type black developers (1) and (S1) obtained in the above Examples B-3 and C-3 and the two-component type black developer (2) obtained in 25 the Comparative Example B-3, the charge levels of toners after stirring for 10 and 300 seconds were measured under conditions of normal temperature and

normal humidity (25°C, 60% RH) and high temperature and high humidity (30°C, 80% RH) using the previously described method of measuring charge levels. Then, numbers from measurement values of two-component blow-off charge levels were rounded off to the first decimal place to make evaluations according to the following criteria. The results are shown together in Table 2.

[0293]

<Electrifiability>

10 AA: Excellent (-20 µC/g or lower)
A: Good (-19.9 to -10.0 µC/g)
B: Usable (-9.9 to -5.0 µC/g)
C: Unusable (-4.9 µC/g or higher)

[0294]

15 (Example B-4)

- Styrene-butylacrylate copolymer resin
(glass transition temperature 70°C) 100 parts by mass
- Magenta pigment (C.I. Pigment Red 114)

20 5 parts by mass

- Exemplary compound (1) 2 parts by mass.

The above described compositions were mixed, and were melt-kneaded by a twin screw extruder (L/D=30). The resulting mixture was cooled, was thereafter roughly ground by a hammer mill and finely ground by a jet mill, and was thereafter classified to obtain magenta colored particles (1) by a grinding method.

For the particle size of the magenta colored particles (1), the weight average particle size was 7.3 μm and the ratio of fines was 5.5% by number.

[0295]

5 As a fluidity improver, 1.5 parts by mass of hydrophobic silica fine powder (BET: 250 m^2/g) treated with hexamethyl disilazane were dry-mixed with 100 parts by mass of the magenta colored particles (1) by a Henshel mixer, whereby a magenta toner (1) of this
10 Example was obtained. In addition, 7 parts by mass of the resulting magenta toner (1) were mixed with 93 parts by mass resin-coated magnetic ferrite carrier (average particle size: 45 μm) to prepare a two-component type magenta developer (1) for magnetic brush
15 development.

[0296]

(Example C-4)

Magenta toner (S1) of Example C-4 was obtained in the same manner as in Example B-4 except that 2 parts
20 by mass of an exemplary compound (S1) was used in place of an exemplary compound (1). The properties of this toner were measured in the same manner as in Example B-3, and the results thereof are shown in Table 2. In addition, two-component type magenta developer (S1) of
25 Example C-4 was obtained in the same manner as in Example B-4 using this toner.

[0297]

(Comparative Example B-4)

A magenta toner (2) of Comparative Example B-4 was obtained in the same manner as in Example B-4 except that an exemplary compound was not used. The 5 properties of this toner were measured in the same manner as in Example B-3, and the results thereof are shown in Table 2. In addition, a two-component type magenta developer (2) of Comparative Example B-4 was obtained in the same manner as in Example B-4 using 10 this toner.

[0298]

<Evaluation>

For the two-component type magenta developers (1) and (S1) obtained in the Examples B-4 and C-4 and the 15 two-component type magenta developer (2) obtained in the Comparative Example B-4, the charge levels of toners after stirring for 10 and 300 seconds were measured under conditions of normal temperature and normal humidity (25°C, 60% RH) and high temperature and 20 high humidity (30°C, 80% RH) using the previously described method of measuring charge levels. Then, numbers from measurement values of two-component blow-off charge levels were rounded off to the first decimal place to make evaluations according to the following 25 criteria. The results are shown together in Table 2.

[0299]

<Electrifiability>

AA: Excellent (-20 $\mu\text{C/g}$ or lower)

A: Good (-19.9 to -10.0 $\mu\text{C/g}$)

B: Usable (-9.9 to -5.0 $\mu\text{C/g}$)

C: Unusable (-4.9 $\mu\text{C/g}$ or higher)

5 [0300]

(Examples B-5, C-5)

Black toners (3) and (S3) of Examples B-5 and C-5 were obtained in the same manner as in Example B-4 except that 2.0 parts by mass of exemplary compounds

10 (1) and (S1) were used respectively, and a carbon black (DBP oil absorption 110 mL/100 g) was used in place of the magenta pigment. The properties of these toners were measured in the same manner as in Example B-1, and the results thereof are shown in Table 2. In addition, 15 two-component type black developers (3) and (S3) were obtained in the same manner as in Example B-4 using these toners.

[0301]

(Comparative Example B-5)

20 A black toner (4) of Comparative Example B-5 was obtained in the same manner as in Example B-4 except that an exemplary compound was not used, and that the carbon black (DBP oil absorption 110 mL/100 g) was used in place of the magenta pigment. The properties of 25 this toner were measured in the same manner as in Example B-1, and the results thereof are shown in Table 2. In addition, a two-component type black developer

(4) of Comparative Example B-5 was obtained in the same manner as in Example B-4 using this toner.

[0302]

<Evaluation>

5 For the two-component type black developers (3) and (S3) obtained in the Examples B-5 and C-5 and the two-component type black developer (4) obtained in the Comparative Example B-5, the charge levels of toners after stirring for 10 and 300 seconds were measured
10 under conditions of normal temperature and normal humidity (25°C, 60% RH) and high temperature and high humidity (30°C, 80% RH) using the previously described method of measuring charge levels. Then, numbers from measurement values of two-component blow-off charge
15 levels were rounded off to the first decimal place to make evaluations according to the following criteria.

The results are shown together in Table 2.

[0303]

<Electrifiability>

20 AA: Excellent (-20 µC/g or lower)
A: Good (-19.9 to -10.0 µC/g)
B: Usable (-9.9 to -5.0 µC/g)
C: Unusable (-4.9 µC/g or higher)

[0304]

25 (Example B-6)

- Polyester resin 100 parts by mass
- Carbon black (DBP absorption 110 mL/100 g)

5 parts by mass

· Exemplary compound (1) 2 parts by mass.

The polyester resin was synthesized as follows:

751 parts of bisphenol A propylene oxide 2 mol adduct,

5 104 parts of terephthalic acid and 167 parts of trimellitic anhydride were poly-condensed with two parts of dibutyltin oxide as a catalyst to obtain a polyester resin having a softening point of 125°C.

[0305]

10 The above described compositions were mixed, and were melt-kneaded by a twin screw extruder (L/D=30). The resulting mixture was cooled, was thereafter roughly ground by a hammer mill and finely ground by a jet mill, and was thereafter classified to obtain black
15 colored particles (5) by a grinding method. For the particle size of the black colored particles (5), the weight average particle size was 7.5 μm and the ratio of fines was 4.7% by number.

[0306]

20 As a fluidity improver, 1.5 parts by mass of hydrophobic silica fine powder (BET: 250 m^2/g) treated with hexamethyl disilazane were dry-mixed with 100 parts by mass of the black colored particles (5) by a Henshel mixer to obtain a black toner (5) of this
25 Example. Further, seven parts of the resultant black toner (5) were mixed with 93 parts by mass resin-coated magnetic ferrite carrier (average particle size: 45 μm)

to prepare a two-component type black developer (5) for magnetic brush development.

[0307]

(Example C-6)

5 A black toner (S5) of Example C-6 was obtained in the same manner as in Example B-6 except that 2 parts by mass of an exemplary compound (S1) was used in place of an exemplary compound (1). The properties of the toner were measured in the same manner as in Example B-
10 1, and the results thereof are shown in Table 2. In addition, a two-component type black developer (S5) was obtained in the same manner as in Example C-6 using this toner.

[0308]

15 (Comparative Example B-6)

A black toner (6) of Comparative Example B-6 was obtained in the same manner as in Example B-6 except that no exemplary compound was used. The properties of this toner were measured in the same manner as in
20 Example B-1, and the results thereof are shown in Table 2. In addition, a two-component type black developer (6) of Comparative Example B-6 was obtained in the same manner as in Example B-6 using this toner.

[0309]

25 <Evaluation>

For the two-component type black developers (5), (S5) obtained in the above Examples B-6, C-6 and the

two-component type black developer (6) obtained in the Comparative Example B-6, the charge levels of toners after stirring for 10 and 300 seconds were measured under conditions of normal temperature and normal
5 humidity (25°C, 60% RH) and high temperature and high humidity (30°C, 80% RH) using the previously described method of measuring charge levels. Then, numbers from measurement values of two-component blow-off charge levels were rounded off to the first decimal place to
10 make evaluations according to the following criteria.

The results are shown together in Table 2.

[0310]

<Electrifiability>

AA: Excellent (-20 µC/g or lower)

15 A: Good (-19.9 to -10.0 µC/g)

B: Usable (-9.9 to -5.0 µC/g)

C: Unusable (-4.9 µC/g or higher)

[0311]

[Table 2]

20 Table 2

Examples	Compound number	Toners number	Particle size distribution	Electrifiability			
				Average particle size (μm)	Ratio of fines (%)	Normal temperature and normal humidity (Q/M)	High temperature and high humidity (Q/M)
				10 seconds	300 seconds	10 seconds	300 seconds
B-1	1	Blue 1	6.8	4.9	AA	AA	AA
C-1	S1	Blue S1	6.9	5.0	AA	AA	AA
B-2	1	Yellow 1	7.1	5.2	AA	AA	AA
C-2	S1	Yellow S1	7.0	5.1	AA	AA	AA
B-3	1	Black 1	7.3	4.9	AA	AA	AA
C-3	S1	Black S1	7.2	5.0	AA	AA	AA
B-4	1	Red 1	7.3	5.5	AA	AA	AA
C-4	S1	Red S1	7.2	5.4	AA	AA	AA
B-5	1	Black 3	6.9	4.8	AA	AA	AA
C-5	S1	Black S3	6.8	4.7	AA	AA	AA
B-6	1	Black 5	7.5	4.7	AA	AA	AA
C-6	S1	Black S5	7.4	4.6	AA	AA	AA
Comparative Example B-1	-	Blue 2	7.0	5.2	C	C	C
B-2	-	Yellow 2	7.2	4.9	C	C	C
B-3	-	Black 2	6.9	5.3	C	C	B
B-4	-	Red 2	7.1	5.1	C	C	B
B-5	-	Black 4	7.0	5.7	C	C	C
B-6	-	Black 6	7.5	4.9	C	C	B

[0312]

(Example B-7 to Examples B-12, C-7 to C-12 and
Comparative Example B-7 to Comparative Example B-12)

First, an image forming apparatus used in the
5 image formation methods of Example B-7 to Examples B-
12, C-7 to C-12 and Comparative Example B-7 to
Comparative Example B-12 will be described. Figure 5
is a schematic explanatory view of the cross section of
an image forming apparatus for carrying out the image
10 formation methods of Examples and Comparative Examples
of the present invention. A photosensitive drum 1
shown in Figure 5 has a photosensitive layer 1a having
an organic photo semiconductor on a substrate 1b, and
is configured to rotate in the direction indicated by
15 the arrow, and its surface is electrically charged at a
potential of about -600 V by a charge roller 2 being a
charging member situated opposite to the photosensitive
drum 1 and contacting and rotating with the drum. As
shown in Figure 5, the charge roller 2 has a metal core
20 2b covered with a conductive elastic layer 2a.

[0313]

Next, the photosensitive drum 1 with its surface
electrically charged is exposed to light 3 and at this
time, on/off operations are performed on the
25 photoconductor by a polygon mirror according to digital
image information, whereby an electrostatic latent
image with the potential of the exposed area being -100

V and the potential of the dark area being -600 V is formed. Subsequently, this electrostatic latent image on the photosensitive drum 1 is reverse-developed and thereby actualized using a plurality of development apparatuses 4-1, 4-2, 4-3 and 4-4, and thus a toner image is formed on the photosensitive drum 1. At that time, the two-component type developers obtained in Examples B-1 to B-6, Comparative Examples B-1 to B-6 and C-1 to C-6 were respectively used as developers to form a toner image with a yellow toner, a magenta toner, a cyan toner or a black toner. Figure 6 is an enlarged sectional view of principal parts of development apparatuses 4 for two-component type developers used at that time.

15 [0314]

Then, the toner images on the photosensitive drum 1 are transferred to an intermediate transfer member 5 contacting and rotating with the photosensitive drum 1. As a result, a four-color toner developed image is formed on the intermediate transfer member 5. A non-transferred toner remaining on the photosensitive drum 1 without being transferred is collected in a residual toner container 9 by a cleaning member 8.

[0315]

25 The intermediate transfer member 5 comprises a metal core 5b as a support and an elastic layer 5a provided thereon as shown in Figure 5. In this

Example, the intermediate member 5 having the metal core 5b coated with the elastic layer 5b with a carbon black as a conductivity producer sufficiently dispersed in nitrile-butadiene rubber (NBR) was used. The degree 5 of hardness of the elastic layer 5b measured in accordance with "JIS K-6301" was 30 degrees, and the volume resistivity was $10^9 \Omega\cdot\text{cm}$. The level of transfer current required for transferring the images from the photosensitive drum 1 to the intermediate transfer 10 member 5 is about $5 \mu\text{A}$, and this level of current was obtained by adding a voltage of +500 V to the metal core 5b.

[0316]

The four-color toner developed image formed on the 15 intermediate transfer member 5 is transferred to a transferring material such as a paper by a transfer roller 7, and is thereafter fixed by a heat-fixation apparatus H. The transfer roller 7 is provided thereon the core metal 7b with the outside diameter of 10 mm on 20 which an elastic layer 7a is formed by coating of a foam of ethylene-propylene-diene based tridimensional copolymer (EPDM) dispersing carbon sufficiently therein as a conductivity producing material. The layer had a volume specific resistance of $10^6 \Omega\cdot\text{cm}$ and a hardness 25 degree of 35° as measured in accordance with "JIS K-6301". In addition, a voltage was applied to this transfer roller 7 to pass a transfer current of $15 \mu\text{A}$

therethrough.

[0317]

In the apparatus shown in Figure 5, a fixation apparatus of heated roll type having no oil coating
5 mechanism shown in Figures 9 and 10 was used in the heat-fixation apparatus H. The both upper and lower rollers of the fixation apparatus used here had surface layers made of fluorine based resin. In addition, the diameter of the roller was 60 nm. The fixation
10 temperature for fixation was 160°C, and the nipping width was set at 7 mm. Furthermore, a transfer residual toner on the photosensitive drum 1, which was collected by cleaning, was transported to a developing device by a reuse mechanism for reuse.
15 [0318]

<Evaluation>

Two-component type developers produced using the toners of Examples B-1 to B-6, C-1 to C-6 and two-component type developers produced using toners of
20 Comparative Examples B-1 to B-6 were used, respectively, to perform printout testing at a printout rate of 8 sheets (A4 size) per minute, supplying the developer, in a monochromatic intermittent mode (namely a mode in which the developing device is stopped for 10
25 seconds for each printout to accelerate the deterioration of a toner in a preliminary operation during restart of the device) at a normal temperature

and normal humidity (25°C , 60% RH) and a high temperature and high humidity (30°C , 80% RH) under the conditions described above, and resulting printout images were evaluated for the following items. The 5 evaluation results are shown together in Table 3.

[0319]

[Evaluation of printout images]

1. Image density

Images were printed out on a predetermined number 10 of normal copying papers (75 g/m^2), and the image density was evaluated according to the level at which the density of the image from the final printout was retained with respect to the density of the initial image. Here, for the measurement of image density, a 15 Macbeth reflective densitometer (from Macbeth Co., Ltd.) was used to measure a density relative to that of the printout image of a white ground of which original density was 0.00.

AA: Excellent (image density from the final printout is 20 1.40 or greater)

A: Good (image density from the final printout is 1.35 or greater and lower than 1.40)

B: Usable (image density from the final printout is 1.00 or greater and lower than 1.35)

25 C: Unusable (image density from the final printout is lower than 1.00)

[0320]

2. Image fog

Images were printed out on a predetermined number of normal copying papers (75 g/m^2), and the image fog was evaluated with a solid white image from the final printout. Specifically, the evaluation was made as follows: the worst value of the reflective density of the white ground after printing and the average reflective density of the paper before printing, as measured using a reflective densitometer (Reflectometer ODEL TC-6DS from Tokyo Denshoku Co., Ltd.), were defined as D_s and D_r , respectively, and (D_s-D_r) was calculated from these values as a fog level to make an evaluation according to the following criteria.

AA: Excellent (fog level is 0% or higher and lower than 1.5%)

A: Good (fog level is 1.5% or higher and lower than 3.0%)

B: Usable (fog level is 3.0% or higher and lower than 5.0%)

C: Unusable (fog level is higher than 5.0%)

[0321]

3. Transferability

Solid black images were printed out on a predetermined number of normal copying papers (75 g/m^2), and the image dislocation level of the image from the final printout was visually observed to make an evaluation according to the following criteria.

AA: Excellent (almost not observed)

A: Good (slightly observed)

B: Usable

C: Unusable.

5 [0322]

In addition, in Example B-7 to Example B-12,
Example C-7 to Example C-12 and Comparative Example B-7
to Comparative Example B-12, occurrences of scars and
sticking residual toners on the surfaces of the
10 photosensitive drum and intermediate transfer member,
and their influence on printout images (matching with
the image forming apparatus) were visually evaluated
after 5000 images were outputted, and as a result,
scars and sticking residual toners on the surfaces of
15 the photosensitive drum and intermediate transfer
member were not observed, and thus matching with the
image forming apparatus was excellent for the system
using two-component type developers of Example B-7 to
Example B-12, Example C-7 to Example C-12. For the
20 system using two-component type developers of
Comparative Examples B-7 to B-12, on the other hand,
sticking toners were observed on the surface of the
photosensitive drum in all cases. In addition, for the
system using two-component type developers of
25 Comparative Examples B-7 to B-12, sticking toners and
surface scars could be observed on the surface of the
intermediate transfer member, and there was a problem

in matching with image formation apparatus such that longitudinally striped defects occurred on the image.

[0323]

[Table 3]

Table 3

Examples	Two-component type developer	Normal temperature and normal humidity			High temperature and high humidity	
		Image density	Image fog	Transferability	Image density	Image fog
B-7	blue 1	AA	AA	AA	AA	AA
C-7	blue S1	AA	AA	AA	AA	AA
B-8	yellow 1	AA	AA	AA	AA	AA
C-8	yellow S1	AA	AA	AA	AA	AA
B-9	black 1	AA	AA	AA	AA	AA
C-9	black S1	AA	AA	AA	AA	AA
B-10	red 1	AA	AA	AA	AA	AA
C-10	red S1	AA	AA	AA	AA	AA
B-11	black 3	AA	AA	AA	AA	AA
C-11	black S3	AA	AA	AA	AA	AA
B-12	black 5	AA	AA	AA	AA	AA
C-12	black S5	AA	AA	AA	AA	AA
Comparative Example B-7	blue 2	C	C	C	C	C
B-8	yellow 2	C	C	C	C	C
B-9	black 2	B	C	B	C	C
B-10	red 2	B	C	B	C	C
B-11	black 4	B	C	C	C	C
B-12	black 6	B	C	B	C	C

[0324]

(Example B-13 to Example B-15, Example C-13 to Example C-15, and Comparative Example B-13 to Comparative Example B-15)

5 For carrying out the image formation methods of Example B-13 to Example B-15, Example C-13 to Example C-15, and Comparative Example B-13 to Comparative Example B-15, the toners obtained in Examples B-1 to B-3, Examples C-1 to C-3 and Comparative Examples B-1 to 10 B-3 were used, respectively, as developers. In addition, for means for forming an image, an image forming apparatus with a commercially available laser beam printer LBP-EX (from Canon Inc.) modified so that it was provided with a reuse mechanism and reset as 15 shown in Figure 7 was used. That is, the image forming apparatus shown in Figure 7 is provided with a system in which a non-transferred toner remaining on the photosensitive drum 20 after the transfer process is scraped off by an elastic blade 22 of a cleaner 21 20 abutting against the photosensitive drum 20, then sent into the cleaner 21 by a cleaner roller, passed through a cleaner reuse 23, and returned to the development device 26 via a hopper 25 by a supply pipe 24 with a carrier screw mounted thereon, and the toner collected 25 in this way is reused.

[0325]

In the image forming apparatus shown in Figure 7,

the surface of the photosensitive drum 20 is electrically charged by a primary charge roller 27. A rubber roller (diameter 12 mm, abutment pressure 50 gf/cm) coated with a nylon resin and having conductive 5 carbon dispersed therein was used for the primary charge roller 27, and an electrostatic latent image with a dark area potential V_D of -700 V and a light area potential V_L of -200 V was formed on the electrostatic latent image-holding member

10 (photosensitive drum 20) by laser exposure (600 dpi, not shown). As a toner carrier, a development sleeve 28 having a roughness degree R_a of 1.1 with the surface coated with a resin having a carbon black dispersed therein was used.

15 [0326]

An enlarged sectional view of the principal part of the development apparatus for one-component type developers used in Example B-13 to Example B-15, Example C-13 to Example C-15 and Comparative Example B-20 13 to Comparative Example B-15 is shown in Figure 8. For conditions for developing electrostatic latent images, the speed of the development sleeve 28 was set at a speed 1.1 times as high as the movement speed of the surface of the photosensitive drum 20 opposite thereto, and the space a between the photosensitive 25 drum 20 and the development sleeve 28 (between S and D) was 270 μm . For the member for controlling the

thickness of the toner, an abutting urethane rubber blade 29 was used. In addition, the set temperature of the heat-fixation apparatus for fixing a toner image was 160°C. Furthermore, for the fixation apparatus, a 5 fixation apparatus shown in Figures 9 and 10 was used.

[0327]

As described above, under the condition of normal temperature and normal humidity (25°C, 60%RH), images were printed out on up to 30,000 sheets at a printout 10 rate of 8 sheets (A4 size) per minute, supplying the toner, in a continuous mode (namely, a mode in which the development device is not stopped, and thereby consumption of the toner is accelerated), and the densities of resulting printout images were measured to 15 evaluate the durability according to the following criterion. In addition, the image from the 10,000th printout was observed to make an evaluation about image fog according to the following criterion. At the same time, situations of the components comprising the image 20 forming apparatus after the durability testing were observed to evaluate matching between each component and the above described toner. The results thereof are shown together in Table 4.

[0328]

25 [Change in image density during endurance]

Images were printed out on a predetermined number of normal copying papers (75 g/m²), and the image

density was evaluated according to the level at which the density of the image from the final printout was retained with respect to the density of the initial image. Here, for the measurement of image density, a

5 Macbeth reflective densitometer (from Macbeth Co., Ltd.) was used to measure a density relative to that of the printout image of a white ground of which original density was 0.00.

AA: Excellent (image density from the final printout is
10 1.40 or greater)

A: Good (image density from the final printout is 1.35 or greater and lower than 1.40)

B: Usable (image density from the final printout is 1.00 or greater and lower than 1.35)

15 C: Unusable (image density from the final printout is lower than 1.00)

[0329]

[Image fog]

Images were printed out on a predetermined number
20 of normal copying papers (75 g/m²), and the image fog was evaluated with a solid white image from the final printout. Specifically, the evaluation was made as follows: the worst value of the reflective density of the white ground after printing and the average
25 reflective density of the paper before printing, as measured using a reflective densitometer (Reflectometer ODEL TC-6DS from Tokyo Denshoku Co., Ltd.), were

defined as D_s and D_r , respectively, and (D_s-D_r) was calculated from these values as a fog level to make an evaluation according to the following criteria.

AA: Excellent (fog level is 0% or higher and lower than 5 1.5%)

A: Good (fog level is 1.5% or higher and lower than 3.0%)

B: Usable (fog level is 3.0% or higher and lower than 5.0%)

10 C: Unusable (fog level is higher than 5.0%)
[0330]

[Evaluation of matching with image forming apparatus]

1. Matching with development sleeve

After the printout testing was completed, the 15 situation of residual toners sticking to the surface of the development sleeve and their influence on the printout image were visually evaluated.

AA: Excellent (not observed)

A: Good (almost not observed)

20 B: Usable (sticking residual toners are observed but the influence on the image is not significant)

C: Unusable (sticking of residual toners is significant, causing unevenness in the image)

[0331]

25 2. Matching with photosensitive drum

Occurrences of scars and sticking residual toners on the surface of the photosensitive drum and their

influence on the printout image were visually evaluated.

AA: Excellent (not observed)

A: Good (scars are slightly observed but no influence
5 on the image)

B: Usable (sticking residual toners and scars are observed but the influence on the image is not significant)

C: Unusable (sticking of residual toners is
10 significant, causing longitudinal striped defects in the image)

[0332]

3. Matching with fixation apparatus

The surface conditions of the fixation film were
15 observed, and the results of surface characteristics and occurrences of sticking residual toners were collectively averaged to evaluate the durability of the film.

[0333]

20 (1) Surface characteristics

Occurrences of scars and flaking on the surface of the fixation film were visually observed and evaluated after the printout testing was completed.

AA: Excellent (not observed)

25 A: Good (almost not observed)

B: Usable

C: Unusable

[0334]

(2) Situation of sticking residual toners

The situation of residual toners sticking to the surface of the fixation film was visually observed and 5 evaluated after the printout testing was completed.

AA: Excellent (not observed)

A: Good (almost not observed)

B: Usable

C: Unusable

10 [0335]

[Table 4]

Table 4

Examples	Toner	Evaluation of printout image				Evaluation of matching with other apparatus		
		Change in image density during endurance		10 thou-sands	30 thou-sands	10 thou-sands	Develop-ment sleeve	Photo-sensitive drum
		Initial	Thou-sand	AA	AA	AA	AA	AA
B-13	blue 1	AA	AA	AA	AA	AA	AA	AA
C-13	blue S1	AA	AA	AA	AA	AA	AA	AA
B-14	yellow 1	AA	AA	AA	AA	AA	AA	AA
C-14	yellow S1	AA	AA	AA	AA	AA	AA	AA
B-15	black 1	AA	AA	AA	AA	AA	AA	AA
C-15	black S1	AA	AA	AA	AA	AA	AA	AA
Comparative Example B-3	blue 2	B	C	C	C	C	C	C
B-14	yellow 2	B	C	C	C	C	C	C
B-15	black 2	A	B	C	C	C	C	C

[0336]

(Example B-16, B-16)

Printout testing was performed, supplying the blue toners (1) and (S1) of Examples B-1 and C-1 respectively, in a continuous mode (namely, a mode in which the development device is not stopped, thereby accelerating consumption of the toner) in the same manner as in Examples B-13 and C-13 except that the toner reuse mechanism of the image forming apparatus of Figure 7 was removed, and the printout rate was set at the level of 16 sheets (A4 size) per minute. The resulting printout images and the matching with the image evaluating apparatus used were evaluated for the same items as in Example B-13 to Example B-15, Example C-13 to Example C-15 and Comparative Examples B-13 to Comparative Example B-15. As the result, satisfactory results were obtained for all the items.

[0337]

[Effect of the Invention]

A polyester according to the present invention is a PHA-type polyester containing a 3-hydroxy-5-(4-carboxyphenyl)alkanoic acid unit represented by the above-mentioned chemical formula (I). The PHA-type polyester, which contains a benzene ring having a carboxyl group on it as a substituting ring at the end of side chain, was not conventionally reported. This invention provides a novel

polyhydroxyalkanoate, in which a carboxyl group that is a functional group usable for various applications has been introduced, and a process for preparing the same. Because of this, this novel

5 polyhydroxyalkanoate is excellent not only in melt-processability but also in biocompatibility thanks to its hydrophilic property; therefore, its applications to flexible members for medical use and others are also being expected.

10 [0338]

In addition, according to the present invention, by adding one or more types of polyhydroxyalkanoate represented by chemical formula (1) as a charge controlling agent in an electrostatic latent image 15 developing toner composition, it makes possible to provide an electrostatic latent image developing toner, which is excellent in chargeability and has improved dispersibility and spentability of the compound in the toner resin; which does not cause image fog but 20 is excellent in transferability even at the time of output at an image forming apparatus, and which can be applied to the electrophotographic process at a highly sophisticated level. The toner of this invention is also characterized by that since the 25 charge controlling agent used in the present invention is colorless or weak in coloring, arbitrary colorants can be selected in accordance

with the hue required for the color toner and the toner does not hinder at all the original hues that dyes and pigments have. Furthermore, since this electrostatic latent image developing toner of the 5 present invention does not contain heavy metals, so it is quite safe and needs not undergo burning treatment thanks to its biodegradability, and therefore it provides substantial industrial effect even from a viewpoint of environmental protection, such as 10 prevention of air pollution and global warming.

[Brief Description of the Drawings]

[Figure 1] A ^1H -NMR spectrum of the polyhydroxyalkanoate obtained in Example A-1.

15 [Figure 2] A ^1H -NMR spectrum of the polyhydroxyalkanoate obtained in Example A-2.

[Figure 3] A ^1H -NMR spectrum of the polyhydroxyalkanoate obtained in Example A-3.

[Figure 4] A ^1H -NMR spectrum of the polyhydroxyalkanoate obtained in Example A-4.

20 [Figure 5] A schematic illustration of the image forming apparatus that is used in Examples B-7 to B-12, Examples C-7 to C-12, and Comparative Examples B-7 to B-12.

[Figure 6] A cross-sectional view showing the 25 main part of the developing equipment for two component developing agent that is used in Examples B-7 to B-12, Comparative Examples B-7 to B-12, and Examples C-7 to

C-12.

[Figure 7] A schematic illustration of the image forming apparatus including a reuse mechanism for toner that is used in Examples B-13 to B-16, Examples C-13 to 5 C-16, and Comparative Examples B-13 to B-15.

[Figure 8] A cross-sectional view showing the main part of the developing equipment for one component developing agent that is used in Examples B-13 to B-16, Examples C-13 to C-16, and Comparative Examples B-13 to 10 B-15.

[Figure 9] An exploded perspective view of the main part of the fixing equipment used in the Examples of this invention.

[Figure 10] An enlarged sectional view of the 15 main part of the fixing equipment that is used in the Examples of this invention.

[Figure 11] A schematic illustration of a blowoff chargometry which measures the amount of charge on toners.

20 [Description of Reference Numerals or Symbols]

1, 20: photosensitive member (electrostatic latent image-holding member)

2, 27: Charge roller

3: Exposure light

25 4, 26: Development apparatus (4-1, 4-2, 4-3, 4-4)

5: Intermediate transfer member

6: Transfer material

- 7: Transfer roller
- 13: Photosensitive drum
- 11, 28: Developer holding member
- 30: Stay
- 5 31: Heating member
 - 31a: Heater substrate
 - 31b: Exothermic member
 - 31c: Surface protective layer
 - 31d: Temperature measurement element
- 10 32: Fixation film
- 33: Heated roller
- 34: Coil string
- 35: Film end portion regulating flange
- 36: Electrical supply connector
- 15 37: Insulating member
- 38: Entrance guide
- 39: Exit guide (separation guide)
- 43: Screen
- 45: Vacuum member
- 20 47: Suction port
- 49: Potentiometer

[Name of the Document] Abstract

[Abstract]

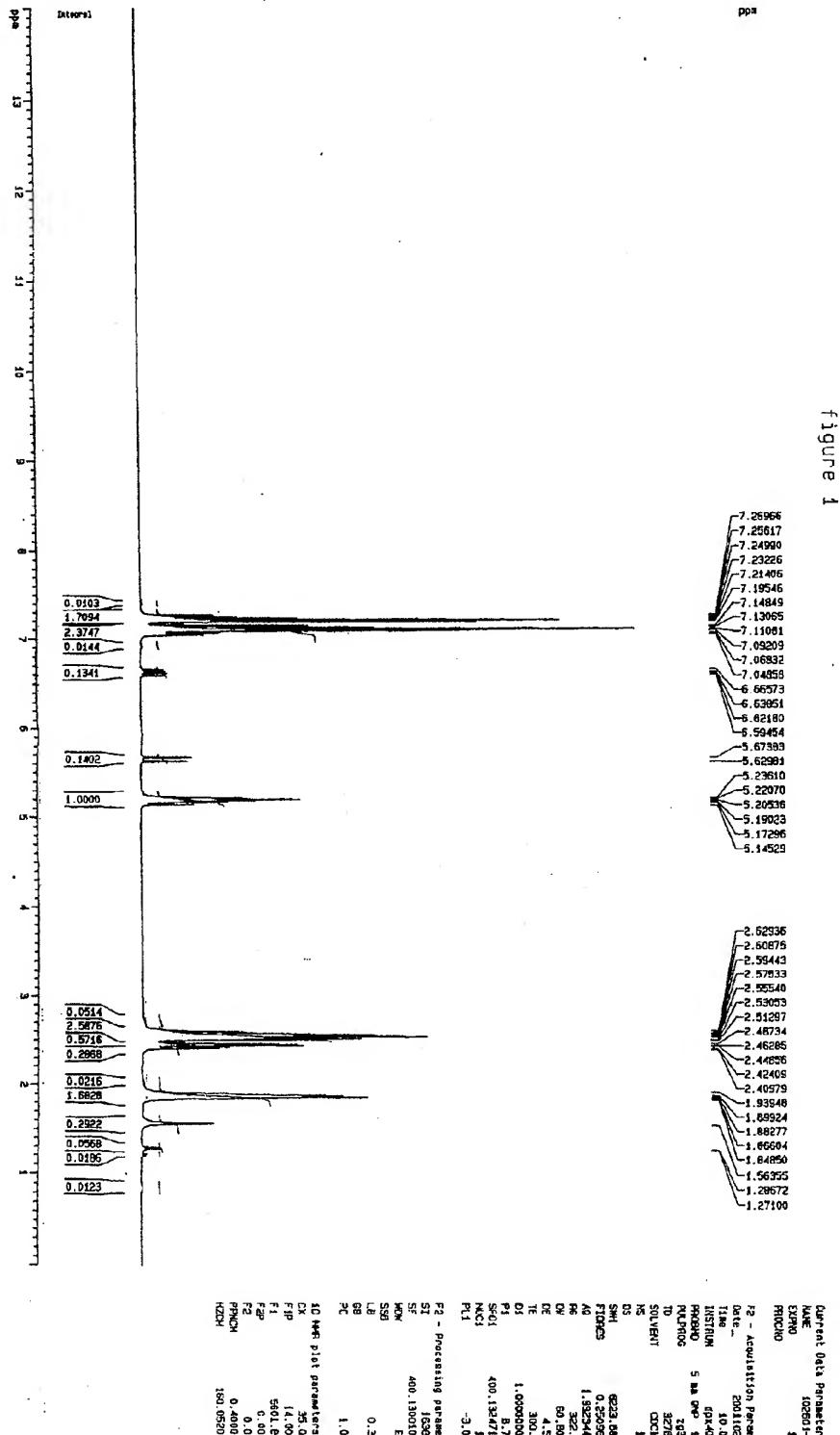
[Problem(s)] It is to provide a polyhydroxyalkanoate type polyester (PHA) having a unit that includes an 5 aromatic ring substituted with a carboxyl group and a process for preparing the same. In addition, the present invention will realize applications of a negatively charged charge controlling agent, being more contributable to preservation of environments and the 10 like, and having high performance (high charge level, quick start of charge, excellent stability with time, and high environmental stability) with improved dispersibility, to the electrophotographic process.

[Means for Solving the Problem(s)] A PHA containing 15 one or more of a unit represented by the chemical formula (1) in the molecule; a process for preparing the PHA by oxidizing and cleaving a double bond portion of a unit represented by the chemical formula (16); a charge controlling agent, which contains the PHA, for 20 controlling a charged state of powder and granular materials; a toner binder which contains the charge controlling agent; an electrostatic latent image developing toner; and an image formation method and an image forming apparatus using these.

提出日 平成14年10月24日
整理番号=4771082 頁: 1/12

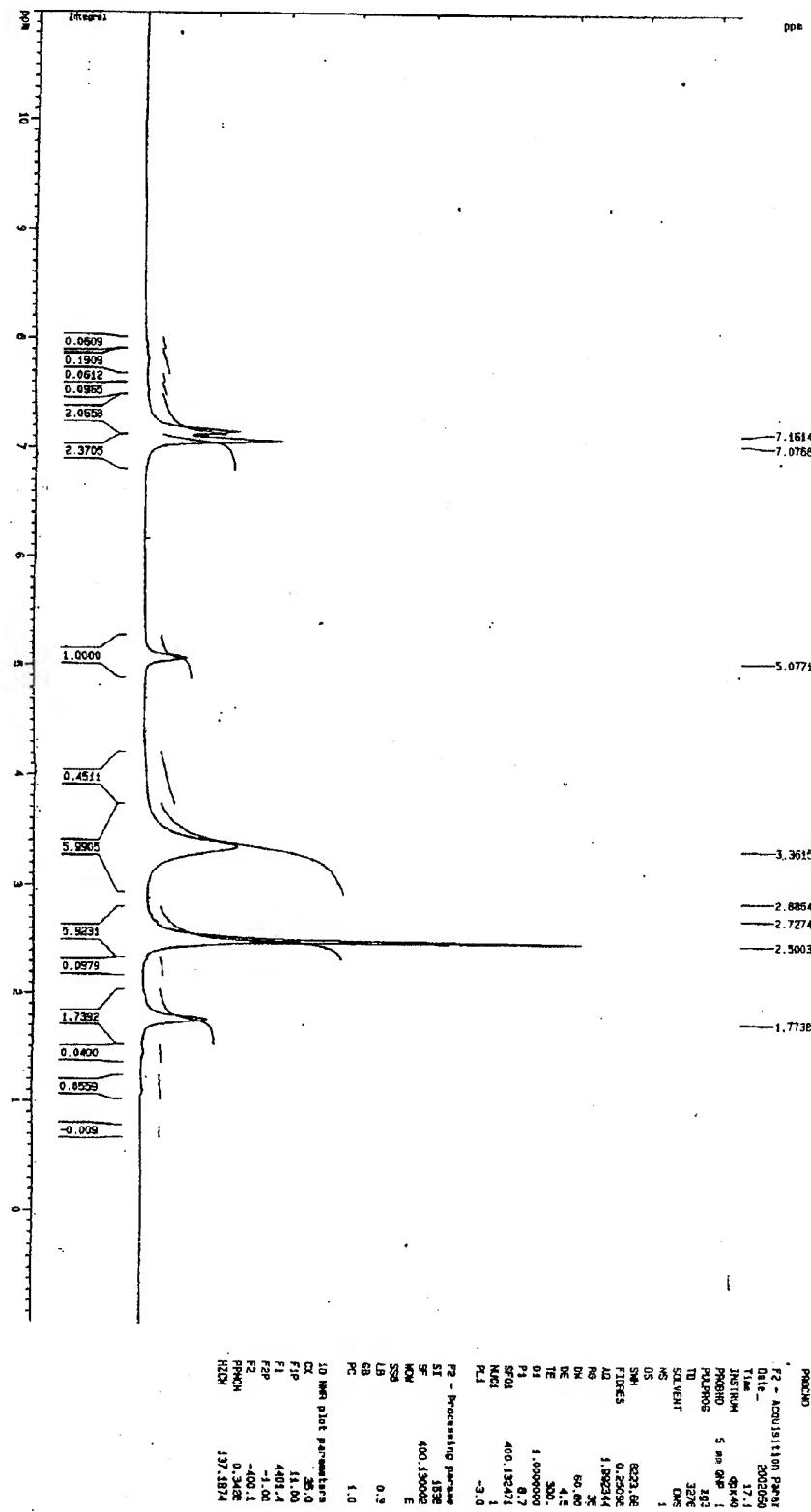
【書類名】 図面 (Name of Document) Drawings

【図1】 Figure 1



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【図2】 Figure 2



整理番号=4771082

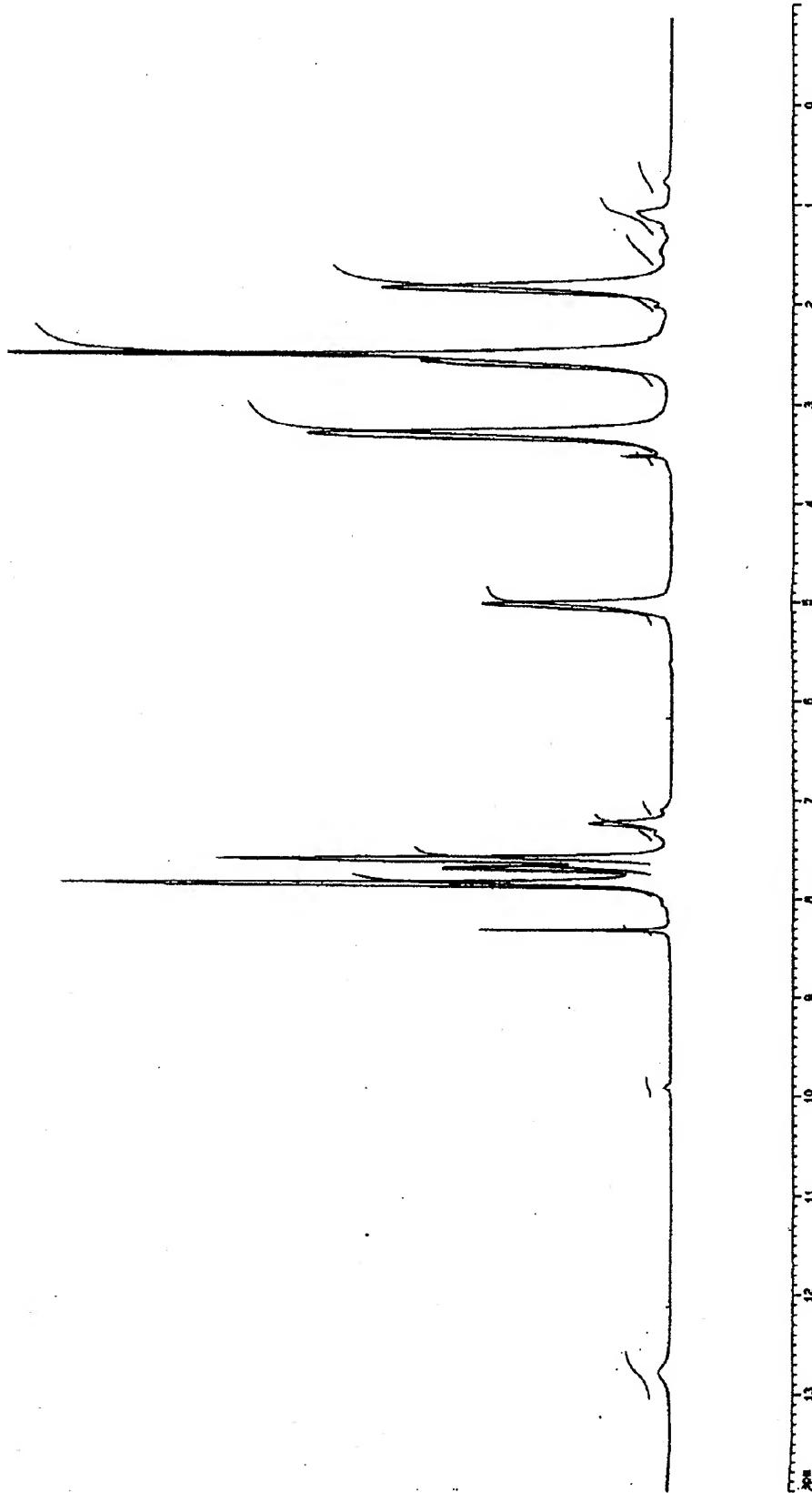
提出日 平成14年10月24日
頁: 3/ 12

【図3】 Figure 3



整理番号=4771082

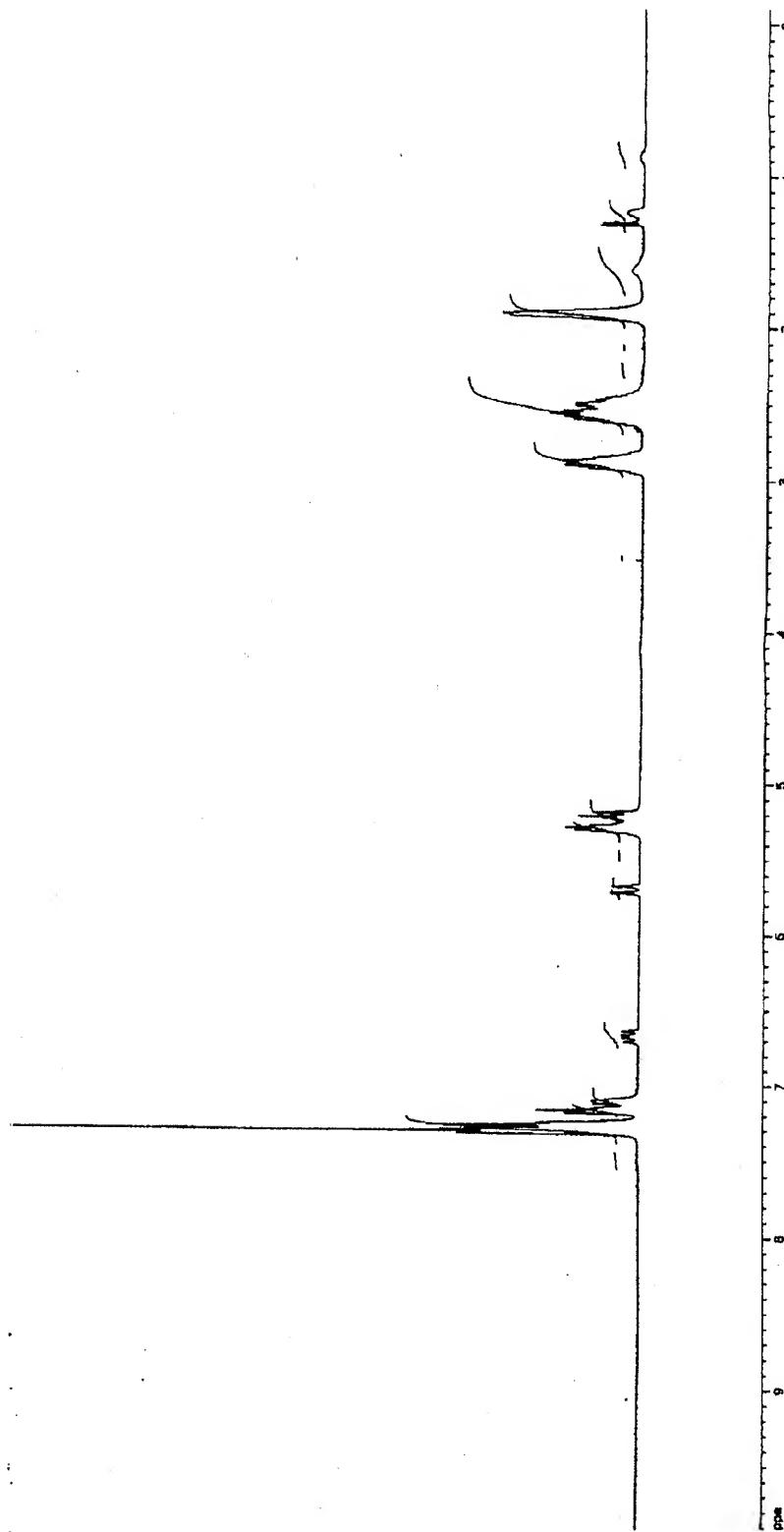
提出日 平成14年10月24日
頁: 4/ 12



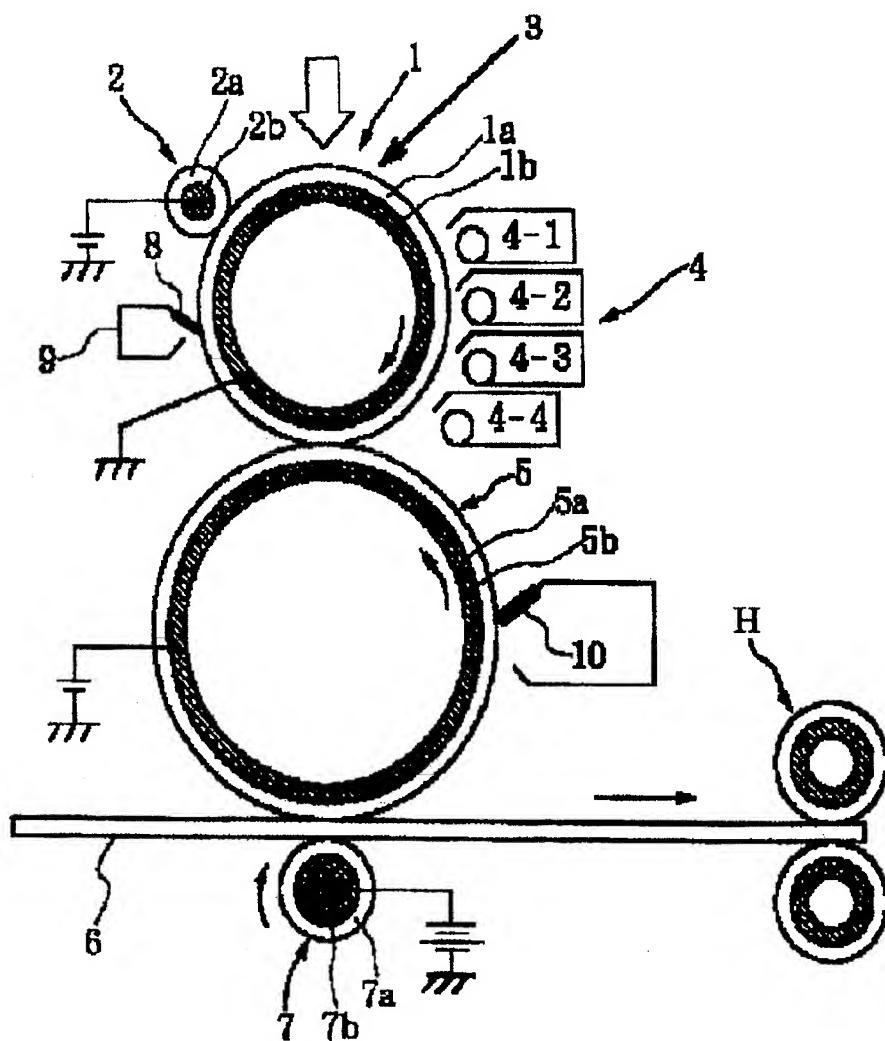
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頁: 5/ 12

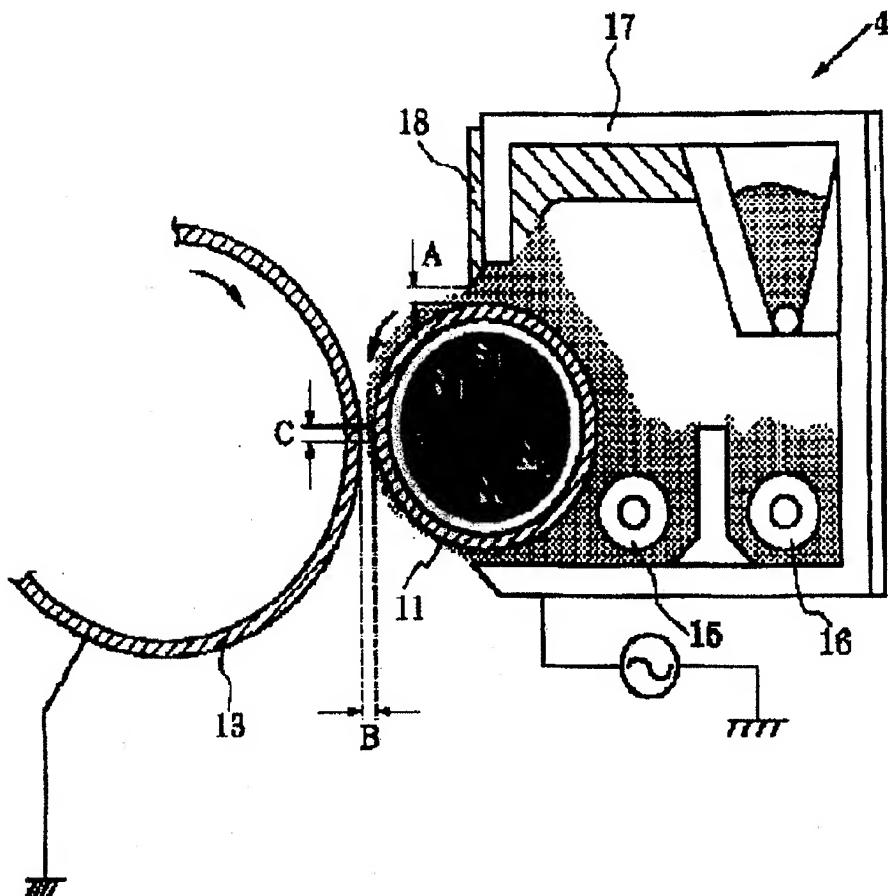
【図4】 Figure 4



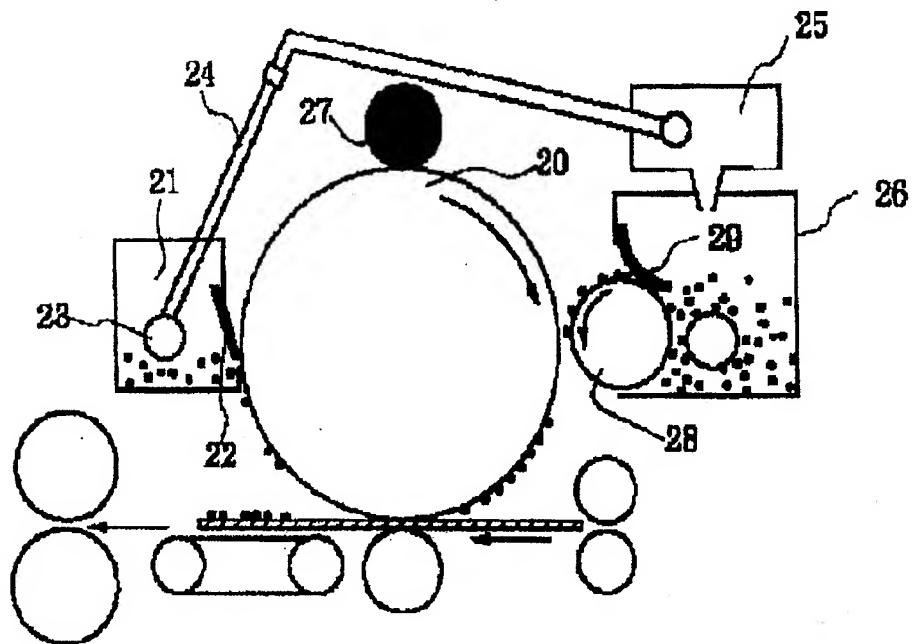
【図5】 Figure 5



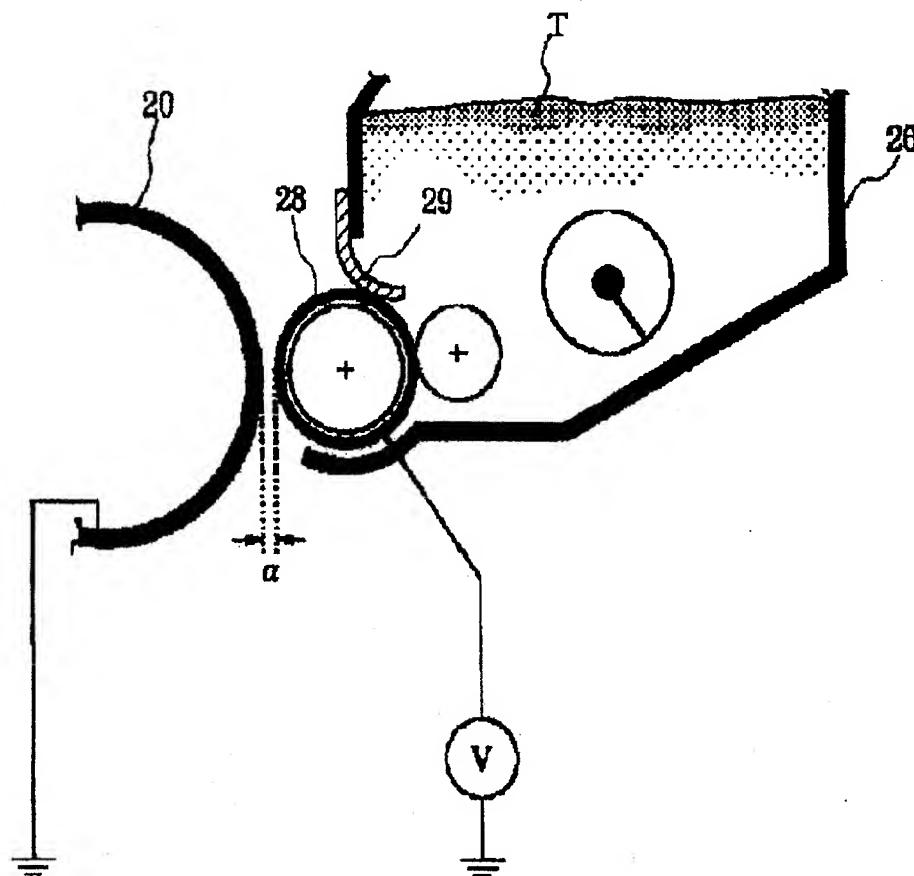
【図6】 Figure 6



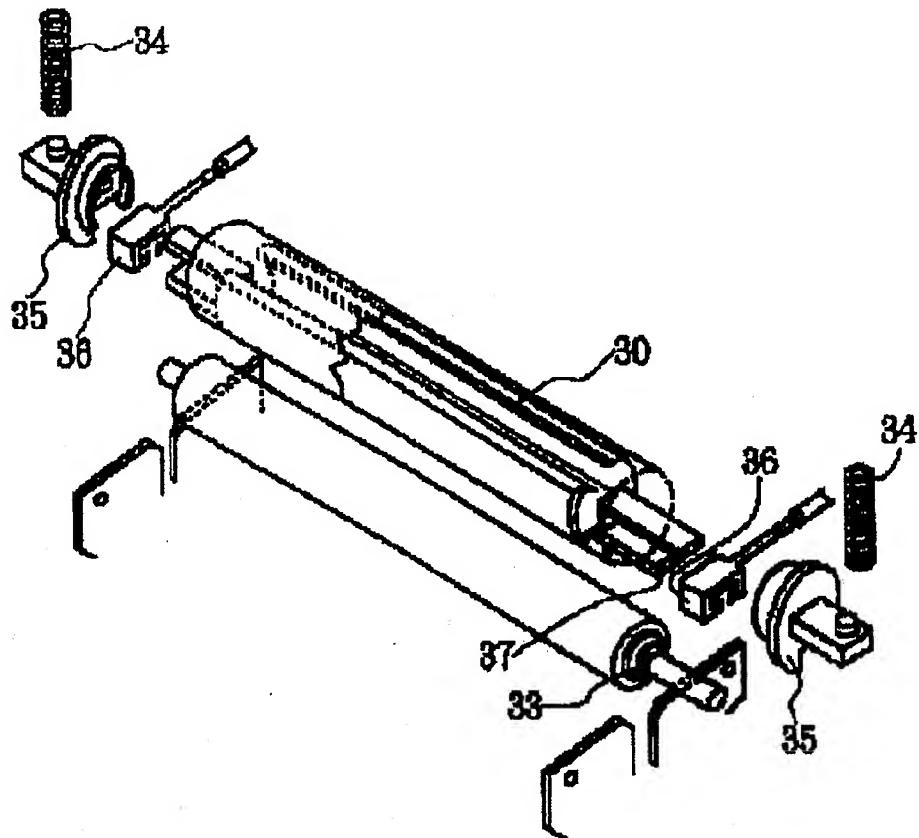
【図7】 Figure 7



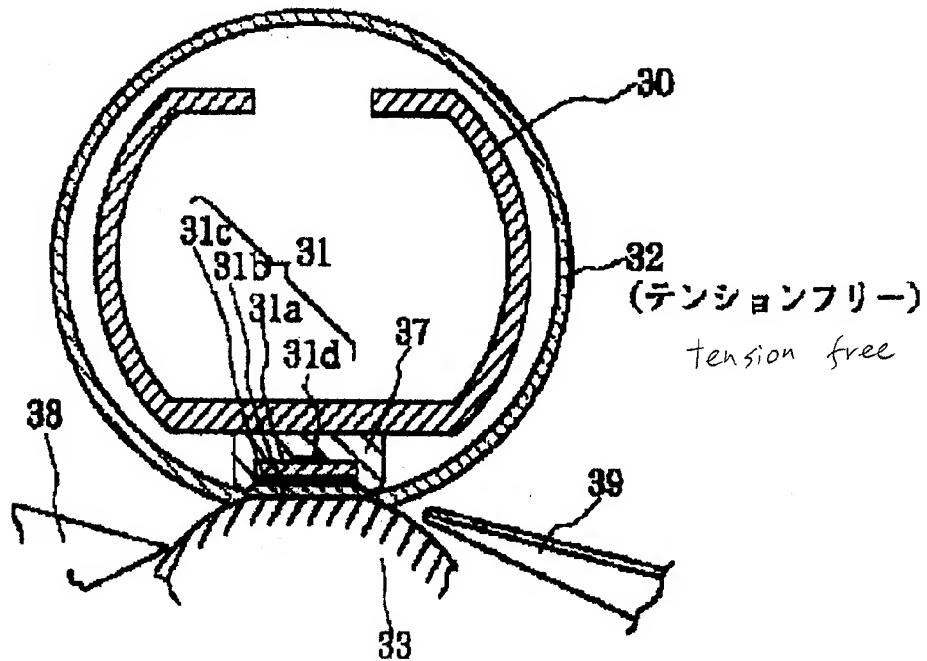
【図8】 Figure 8



【図9】 Figure 9

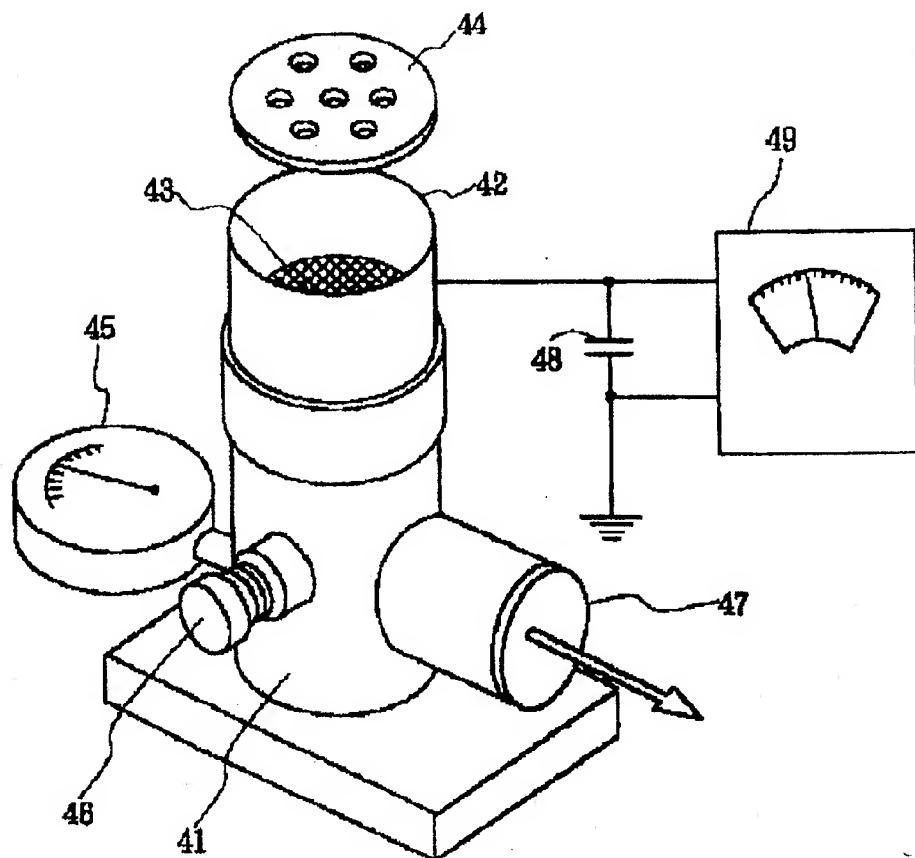


【図10】 Figure 10



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【図11】 Figure 11



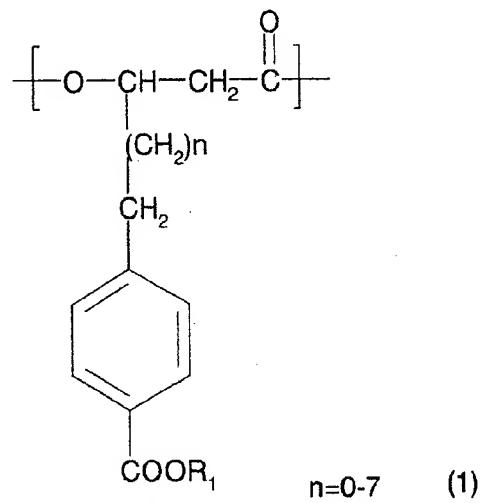
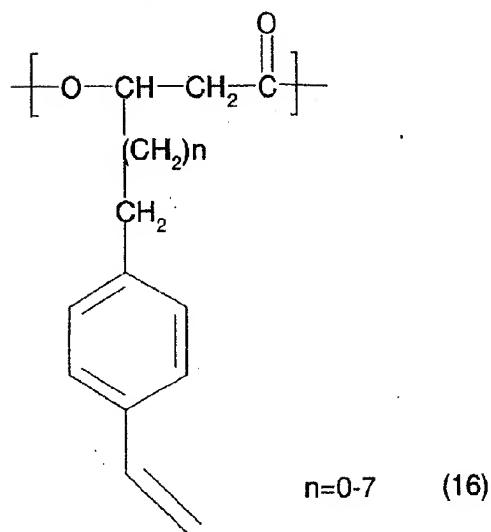
【書類名】 要約書

【要約】

【課題】 カボキル基置換芳香環を含むユニットを有するポリヒドロシリカノエート型ポリエステル(PHA)及びその製造方法を提供する。また、環境の保全等への寄与がより高く、かつ高性能(高帯電量、帯電の立ち上がりが早い、経時安定性に優れる、環境安定性が高い)で分散性の改良された負帯電性の荷電制御剤の電子写真プロトタイプへの応用を実現する。

【解決手段】 分子中に化学式(1)に示すユニットを1ユニット以上含むPHA、化学式(16)に示すユニットの二重結合部分の酸化開裂による、前記PHAの製造方法、該PHAを含む、粉粒体の荷電状態を制御する荷電制御剤、該荷電制御剤を含んでなるトナーパインダー、静電荷像現像トナー、それらを使用する画像形成方法ならびに装置。

【化1】

 $n=0-7$  $n=0-7$ (nは整数; R₁は H, NaまたはK; 各ユニット毎に独立)

【選択図】 なし